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DEVELOPMENT AND TESTING OF AN AIR MONITORING SYSTEM

RESEARCH TRIANGLE INSTITUTE

PREPARED FOR
ENVIRONMENTAL PROTECTION AGENCY

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Instrumentation for the measurement of ozone, sulfur compounds (sulfur dioxide, hydrogen sulfide, total sulfur), nitric oxide, nitrogen dioxide, hydrocarbons (total hydrocarbon, methane, non-methane hydrocarbon) and carbon monoxide in ambient air were included in the program. The evaluation of each instrument included in the program was a systematic comparison of its ability to obtain reliable data with emphasis placed on implementation, if possible, of design changes to instrumentation that could not meet the operational requirements specified for this program.

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by

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This report has been reviewed by the Environmental Protection Agency and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

ABSTRACT

The purpose of this contract was to test and evaluate instrumentation based on specified measurement principles selected for the Regional Air Pollution Study (RAPS), where an extensive network of air monitoring stations equipped with state-of-the-art monitoring instrumentation and sophisticated data acquisition and computer processing systems will be required. The primary objective of the program was to equip an experimental trailer with selected instrumentation and to evaluate these instruments at a non-urban site to: determine if the monitors selected for the study can meet the required performance specifications or need to be modified; determine the operating environment needed to obtain optimum performance from these monitors; evaluate the latest calibration techniques and select calibration procedures to provide the most reliable measurements; and recommend, based on the results of the evaluation program, instrumentation for use in the RAPS program.

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Appreciation is expressed to Messrs. Stevens, Clark, Baumgardner and others of the Field Methods Development Section for their cooperation and assistance during this program.

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1.0 INTRODUCTION

1.1 BACKGROUND AND OBJECTIVES

During the past five (5) years the Environmental Protection Agency has been participating in a demanding instrument development program. Instrumentation based on newly developed measurement principles, such as chemiluminescence, flame photometry, gc-flame photometry, and gc-flame ionization, have been developed and marketed by various manufacturers. Improvements and modifications to instrumentation based on these measurement principles are constantly occurring. Previous field studies[1,2,3] conducted to evaluate some of these analyzers and to compare them to classical measurement principles, such as colorimetry, coulometry, and conductivity, have shown the need for intensive evaluation of new instrumentation for monitoring atmospheric pollutants. In most cases where prototype or first production models of an ambient air analyzer were evaluated, excessive failures occurred which seriously impaired the analyzer's performance. In every case these failures resulted from electronic and/or flow problems and interferences, such as water vapor, interferent gases, vibrations, etc., that could be solved by engineering modifications. This observation indicates that important output requirements of an evaluation program are to point out deficiencies, to document required engineering modifications, and to feed back this information to manufacturers and other interested parties sothat future procurements of similar equipment can incorporate these modifications and/or changes.

During the Regional Air Pollution Study (RAPS) to be conducted in St. Louis, Missouri, an extensive network of air monitoring stations equipped with state-of-the-art monitoring instruments and automatic data acquisition systems will be established. Prior to this, it was deemed necessary to equip an experimental trailer with the latest instrumentation and to evaluate these instruments at a non-urban site to:

- determine whether these new monitors can adequately measure concentrations of H_2S, SO_2, CO, NO, NO_2, NO_x, O_3, THC, CH_4, and non-methane hydrocarbons in a typical non-urban location;
- determine if the monitors selected for this study can meet the required performance specifications or need to be modified;
- determine the operating environment needed to obtain optimum performance from the monitors;
- evaluate the latest calibration techniques and select calibration procedures to provide the most reliable measurements; and
- recommend, based on the results of the evaluation program, instrumentation for use in the RAPS program.

The objective of this program was to test and evaluate instrumentation based on the specified measurement principles selected for the RAPS Program with emphasis being placed on implementation, if possible, of design changes to instrumentation that cannot meet the operational requirements specified for the objectives of the program.

1.2 EXPERIMENTAL APPROACH

An environmentally controlled mobile laboratory was used to house the instrumentation, data acquisition system, on-line computer, and supporting laboratory equipment required to complete this program. Figure 1.1 shows two internal views of the mobile laboratory, including instrumentation and the data acquisition and processing equipment. These facilities are described in detail in Section 2.0 and includes a description of the mobile laboratory, the ambient air sampling system, the data acquisition system, an on-line computer for processing of data in real-time, and a general discussion of the automatic calibration technique, mode switches, and computer programs utilized to process the data in real-time.

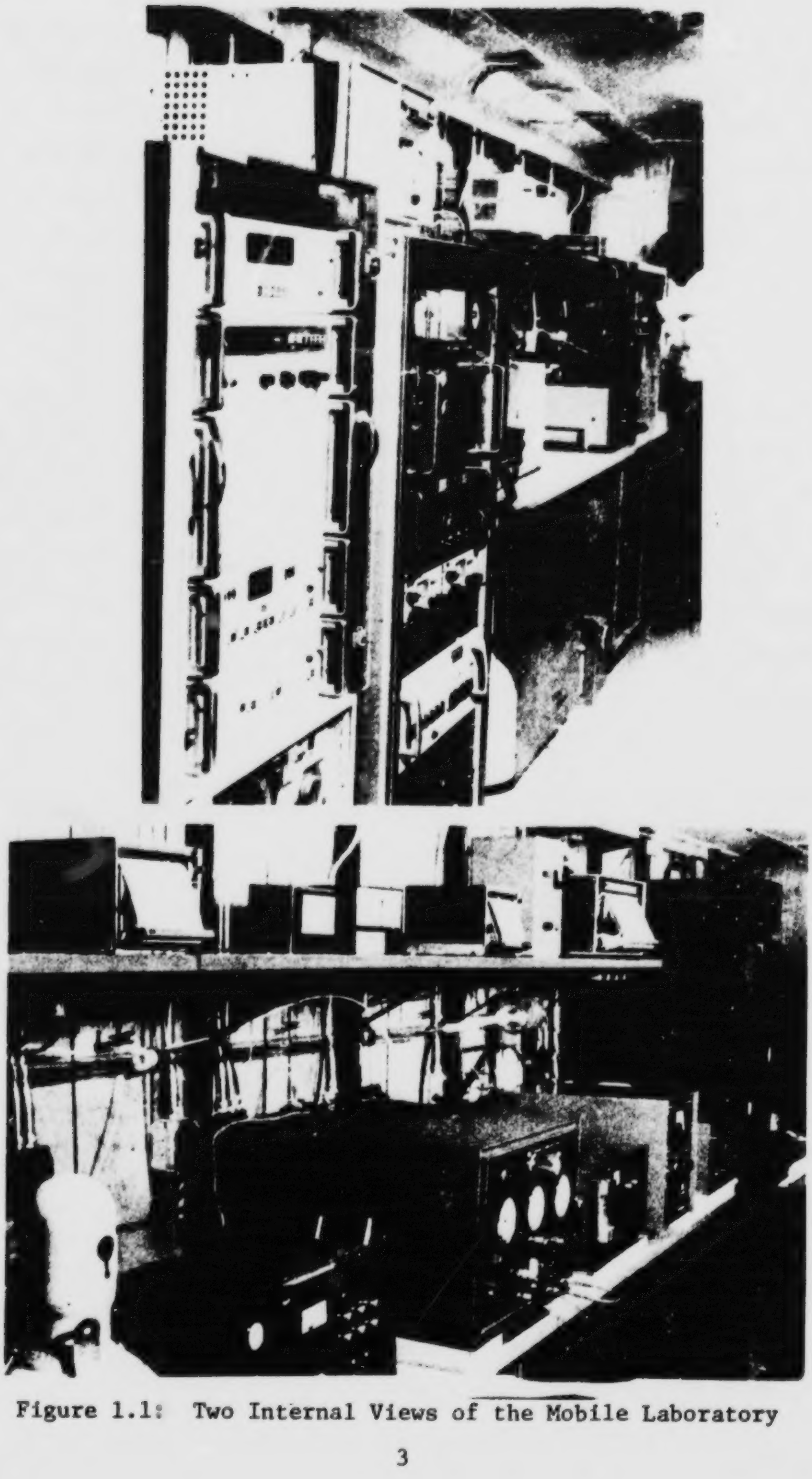

Figure 1.1: Two Internal Views of the Mobile Laboratory

Criteria for selection of instruments and the test plan are presented in Section 3.0. The gas analyzers under evaluation are described in Section 4.0. To expedite the presentation, a standard format was followed for each analyzer and is presented in two parts. Part I includes the following: (1) principle of operation, (2) physical characteristics, (3) gas flow system, (4) detector system, and (5) signal processing. Part II includes the operational summary for the evaluation period, failures, operation, calibration, maintenance requirements, and other pertinent data.

Instrument evaluation procedures, including definitions and test procedures, are presented in Section 5.0. The calibration schedule varied depending on the test plan and evaluation procedure being performed. Calibration procedures used during this study are given in Section 6.0. A summary of instrument performance is presented in Section 7.0 and includes results of the evaluation tests, operational summary, and subsystem component evaluation. Recommendations for selection of instrumentation for the RAPS Program are given in Section 8.0, and recommended calibration, operational, and maintenance procedures are presented in Appendices A, B, and C, respectively. Graphical presentations of zero and span drift for each analyzer evaluated are presented in Appendix D. Computer output formats are presented in Appendix E.

2.0 DESCRIPTION OF FACILITIES

2.1 SHELTER/ENVIRONMENTAL CONTROL

The semi-mobile environmental monitoring laboratory owned by Research Triangle Institute and previously described in the final report for Contract CPA 70-101, "Field Evaluation of New Air Pollution Monitoring Systems"[4], was used to provide the housing and environment required for this evaluation program. This facility contained the necessary structural and electrical facilities and sufficient interior space for housing all the sensors. The environmental control system was capable of maintaining the interior temperature to within ± 4°F within the range 60-90°F. For this evaluation program the semi-mobile environmental monitoring laboratory was located on the Research Triangle Institute's campus in Research Triangle Park, North Carolina. Figure 2.1 shows the mobile laboratory on location at Research Triangle Institute.

2.2 AMBIENT AIR SAMPLING SYSTEM

The ambient air sampling system utilized in the program was constructed of 1-inch (0.4 cm) O.D. pyrex glass and consisted of a cane to prevent moisture and particulates from setting into the inlet; a particulate trap to remove large suspended particulate; six 1.5-meter sections of glass manifold--each section having four sampling ports; and a blower. Ambient air was aspirated through the manifold at a rate of approximately 3 CFM. Sampling ports made of 12/5 ball-and-socket joints were used for each hookup of instrument sample inlet lines which were all Teflon. A diagram of the manifold system is shown in Figure 2.2.

An experiment was conducted to determine possible wall losses of pollutants on the manifold surfaces of glass and teflon. Ozone was chosen as the pollutant for investigation due to its reactivity. Two chemiluminescent gas phase ozone meters were installed in the mobile laboratory at each end and calibrated simultaneously. Immediately after calibration one analyzer was connected to the first sampling port on the manifold and

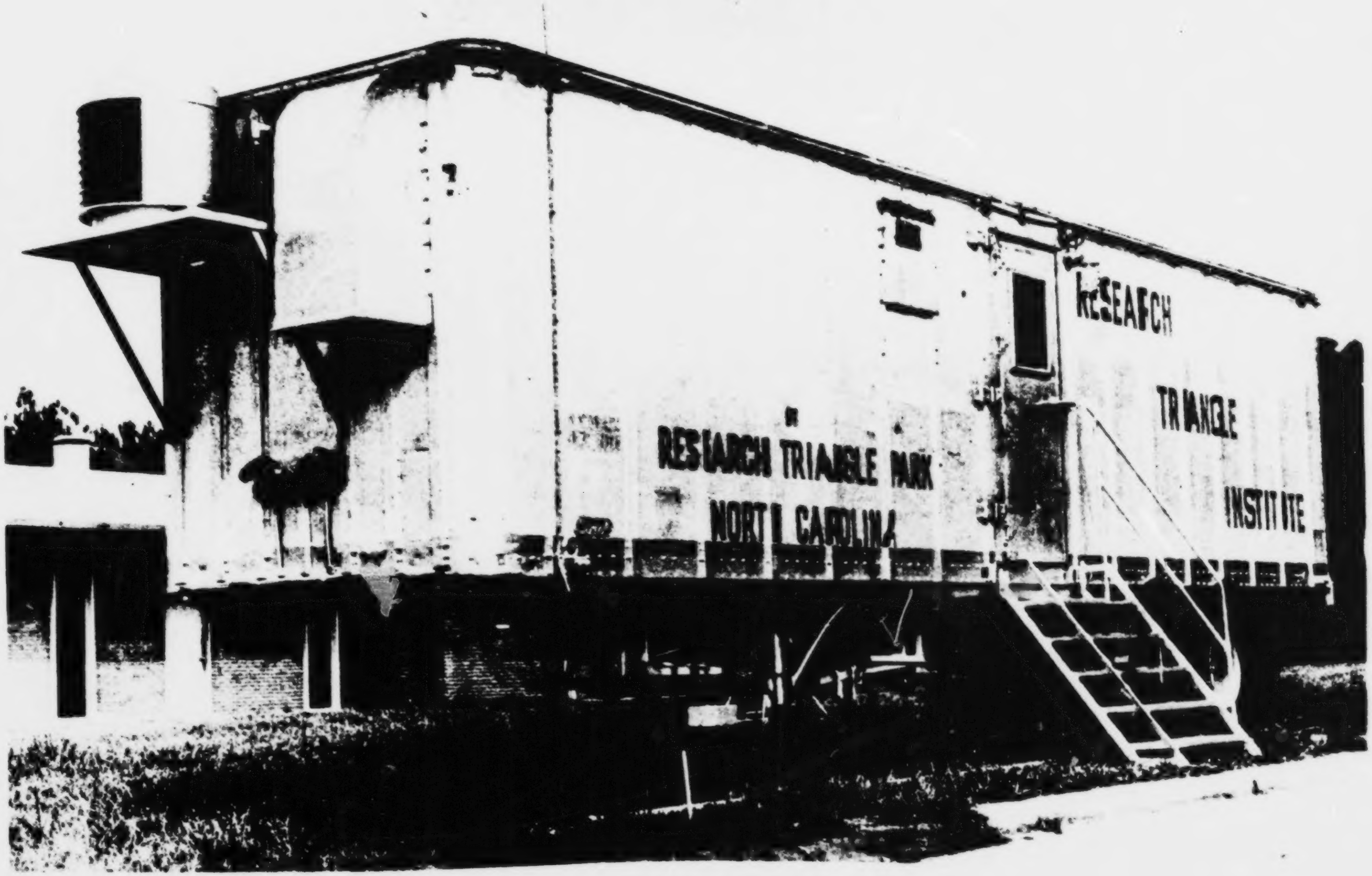
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Figure 2.1. External View of Mobile Laboratory

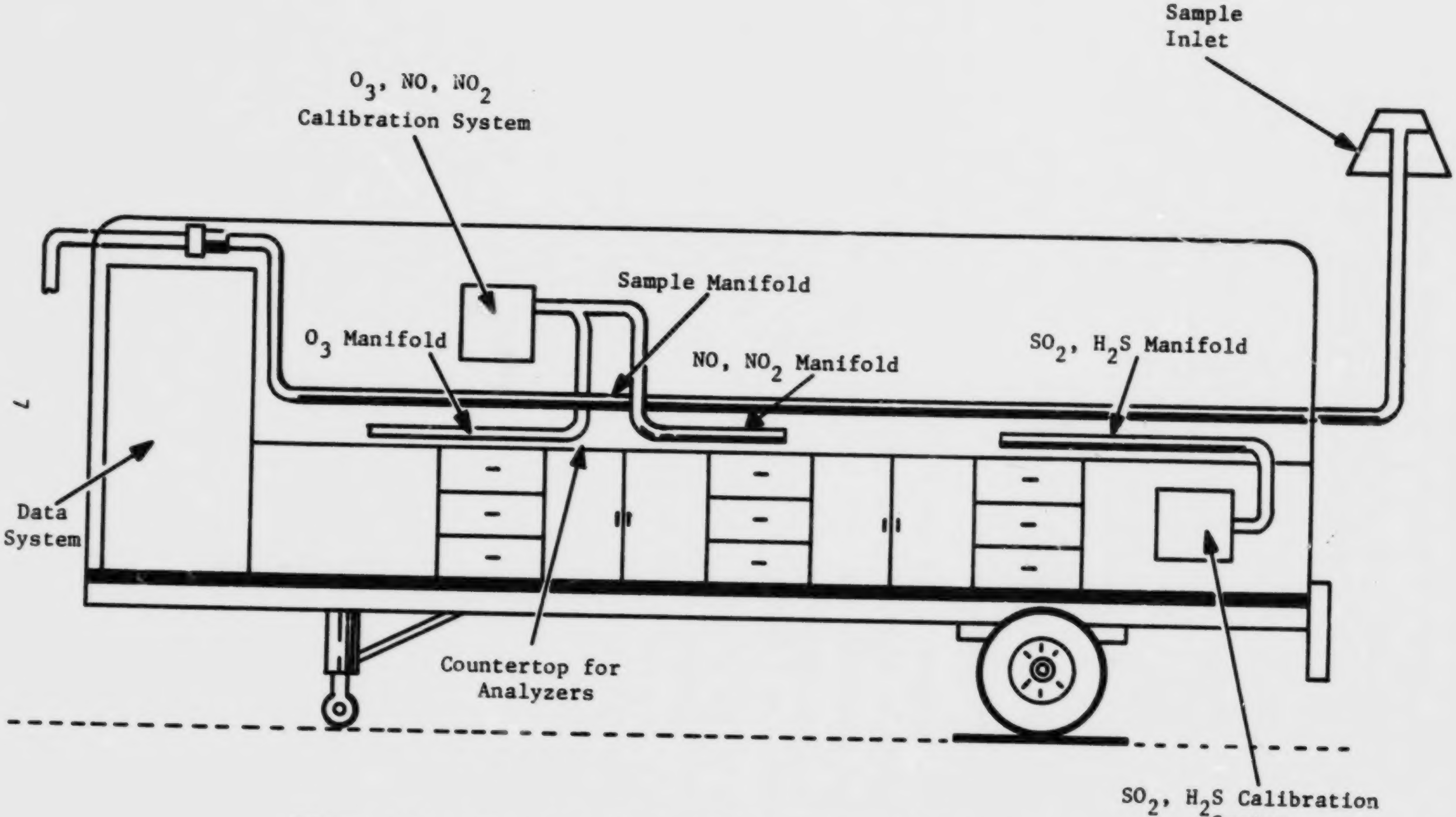

Sample Inlet
O$_3$, NO, NO$_2$ Calibration System
Sample Manifold
O$_3$ Manifold
NO, NO$_2$ Manifold
SO$_2$, H$_2$S Manifold
Data System
Countertop for Analyzers
SO$_2$, H$_2$S Calibration System

Figure 2.2. Diagram of Air Sampling System and Calibration Manifolds

the other analyzer connected to the last sampling port on the manifold some 9 meters away. Ozone concentration measurements were made at both sampling locations on ambient air and on ambient air spiked with ozone generated using an ultraviolet lamp for a period of four hours. Examination of the data indicated that the two measurements were identical down to the part-per-billion level and that ozone was not being destroyed in the manifold under the conditions the air sampling system was being operated. Under these conditions it is very unlikely that other pollutants of interest, such as SO_2, NO, NO_2, THC, NMHC, and CO, are being destroyed due to wall effects in the air sampling system.

2.3 DATA ACQUISITION AND PROCESSING OF DATA

2.3.1 Data Acquisition System

The basic purpose of the data acquisition system was to automatically acquire and record in digital form the output signals derived from the gas analyzers under evaluation and their associated instrument status mode switches. The data acquisition system used in the RTI mobile laboratory basically consists of a Hewlett-Packard 2015H data system, modified and expanded to meet the requirement of a flexible instrument evaluation program. A block diagram of the system as it now stands is shown in Figure 2.3.

Analog signals from the gas analyzers and instrument status switches enter the system by means of an external junction box affixed to the side of the rack panel cabinets. From the input junction box, signals are carried to the sensor coupler for signal conditioning. This unit houses the necessary bridge circuits, scaling networks, bias voltages, etc., which are utilized in converting or modifying the sensor output signal to forms or levels more suitable for recording. Up or down scaling of the signals is sometimes required in order to match the input signal requirements of the analog recorders. In addition, filter networks are incorporated where it is necessary to smooth the signal in order to obtain sampled data that are representative of the preceding sampling interval.

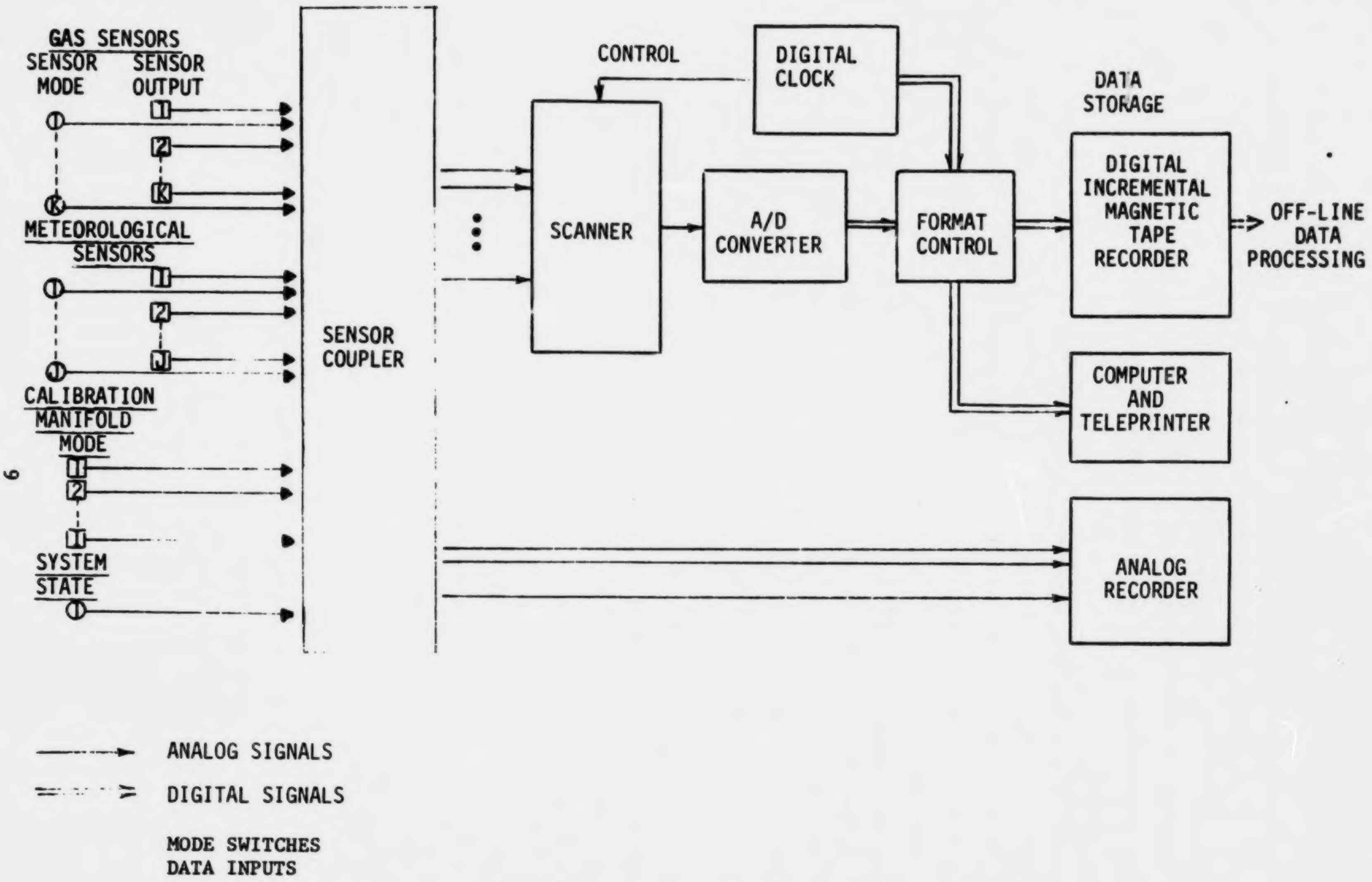

GAS SENSORS
SENSOR MODE
SENSOR OUTPUT
METEOROLOGICAL SENSORS
CALIBRATION MANIFOLD MODE
SYSTEM STATE
SENSOR COUPLER
CONTROL
DIGITAL CLOCK
SCANNER
A/D CONVERTER
FORMAT CONTROL
DATA STORAGE
DIGITAL INCREMENTAL MAGNETIC TAPE RECORDER
OFF-LINE DATA PROCESSING
COMPUTER AND TELEPRINTER
ANALOG RECORDER
ANALOG SIGNALS
DIGITAL SIGNALS
MODE SWITCHES
DATA INPUTS

Figure 2.3. Functional Diagram of Data Acquisition System

A plug-in card is provided for each signal or data channel in which the scaling and filtering networks are incorporated. There are two signal outputs for each channel. One is tied into the digital recording system, and the other into the analog-monitoring or recording system through a front-panel-located patch panel. Isolation is provided between each of the outputs so that on-line tests may be made without disturbing the digital recording system.

From the signal conditioning unit, the analog signals are passed to the digital recording system for recording on magnetic tape. This system, a Hewlett Packard Model 2015H, consists of a scanner capable of accepting up to 200 floating inputs. For this evaluation program, only 65 active channels were needed to monitor sufficiently all the necessary parameters. After passing through the scanner the analog signals are converted to digital numbers by means of a digital voltmeter. The particular model used is a conventional 5-1/2 digit, autoranging model, capable of measuring dc voltage levels from 1.0 volt full scale to 100 volts full scale with an accuracy of 0.01%. Resolution on the lowest scale is 6 digits, yielding a resolution of 10 μV on the most sensitive scale. System control is accomplished by a clock controller unit, the purpose of which is to supply timing pulses and a BCD representation of time to the remaining system. This time code is entered as the first word in each scan, which is days, hours and minutes.

The BCD output of the digital voltmeter along with the time from the clock and a channel indicator from the scanner are input to a tape coupler which feeds the data to the tape deck with the proper accompanying control signals for interrecord gapping and end of files.

Manual data such as instrument mode or status are introduced into the system via manual data entry channels. By utilizing codes, the status or operational mode information was placed in the respective channels and used in the data processing phase to indicate the operational status of the respective sensors being evaluated at any point in time. The manual data entry modes shown in Table 2.1 were those used to describe instrument operational status.

TABLE 2.1 INSTRUMENT OPERATIONAL MODES

Output Symbol	Mode Switch Setting	Operating Condition
	0	Measure - - - Valid Ambient Data
C	1	Calibration - Stabilizing
A	2	Calibration - Zero Averaging
B	3	Calibration - Multi-point Averaging
T	4	Routine Test Procedures
X	5	Offline - - - Not Setup or Available
Q	6	Awaiting Repair
R	7	Repair
L	8	Awaiting Maintenance
M	9	Maintenance
99999 or $$$$		Data Not Available

The auxiliary output of the tape coupler of the data acquisition system is capable of feeding voltage data directly to a column printer or to an on-line computer. This type of system is a satisfactory arrangement, although not ideal, in that it allows data to be fed to the computer; yet the computer does not control the system. For the instrument evaluation program this feature was not a handicap in that real-time data could be obtained from the on-line computer and also processed from magnetic tapes on a large computer.

The manual data inputs presented in Table 2.1 were also used to facilitate an automatic calibration procedure in which calibration concentrations in $\mu g/m^3$ were entered directly on magnetic tape or input to the computer via a teletype keyboard. The calibration concentration data, when combined with the instrument voltage output and the appropriate mode switch status information, can be used to automatically compute a transfer function which relates voltage output to pollutant concentration. This equation then is used for processing the data. A stripchart recording and a computer printout demonstrating the automatic calibration procedure are presented in Figures 2.4 and 2.5, respectively.

2.3.2 On-Line Computer

One of the major requirements for this instrument evaluation program was the need for immediate readout or processing of data in quasi-real time to assist in early identification of weaknesses and/or degradation of analyzer performance. To do this required the use of an on-line computer. This feature was accomplished by installing a Hewlett Packard 2100A computer in the mobile van and coupling it to the output of the data acquisition system described in the preceding section.

The software program written for the HP-2100A computer can effectively be used to process data for up to 20 instruments at one time, the limiting factor here being the size of the memory core (8 k). Instrument names, along with the channel number (on the data acquisition system) of the data and status for that instrument are input quantities, which are read into the computer at the beginning of program execution. This allows ease of reconfiguring the system, adding or deleting instruments, changing calibration equations coefficients, etc. The program monitors the instrument outputs, as they are scanned every 5 minutes, and converts the voltage reading obtained to a concentration in ppm or $\mu g/m^3$ by use of an equation of the form

$$C = A\ V_{OUT} + B$$

where

C = concentration in ppm or $\mu g/m^3$,
A = slope of calibration curve,
V_{OUT} = analyzer voltage output, and
B = intercept of calibration curve.

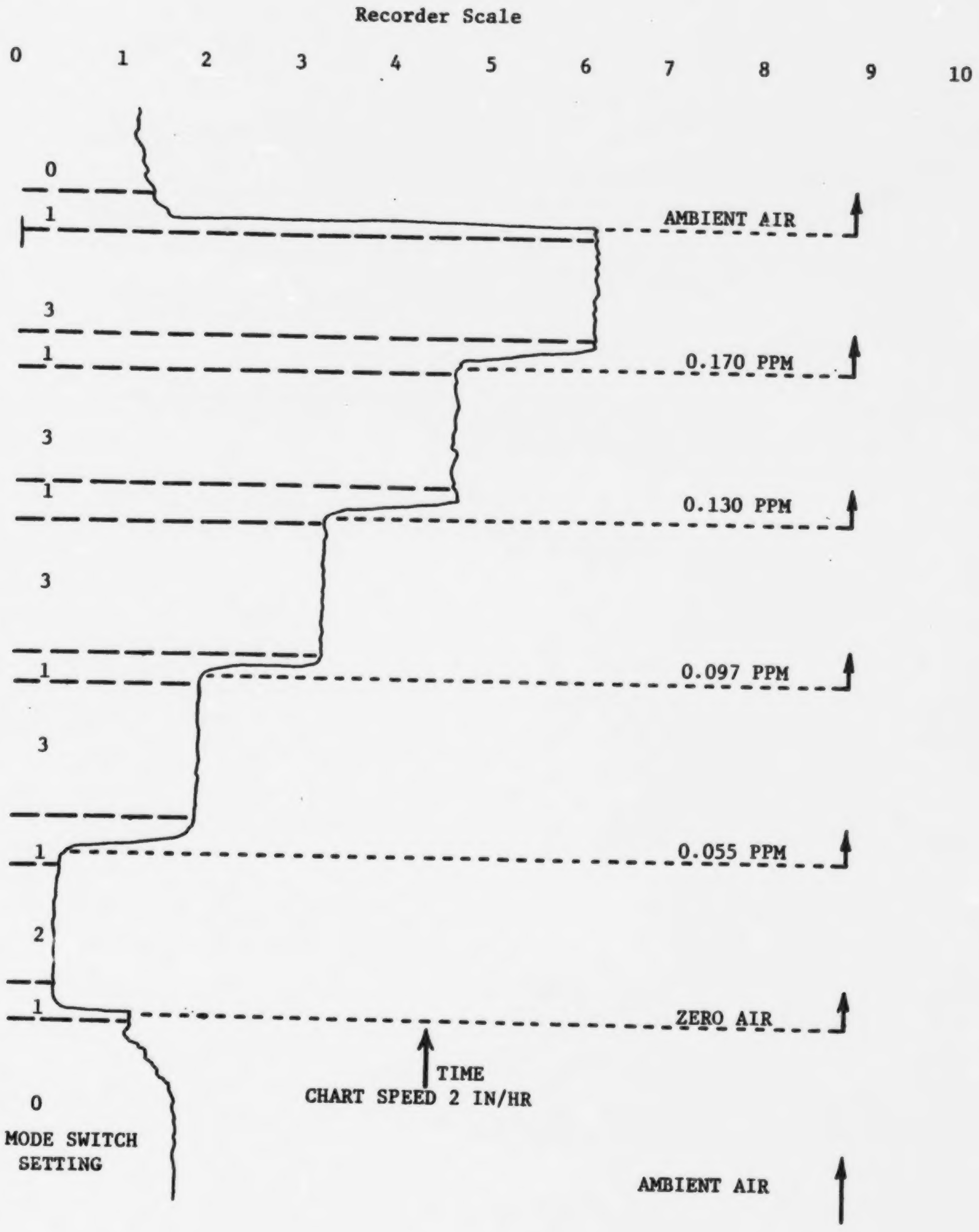
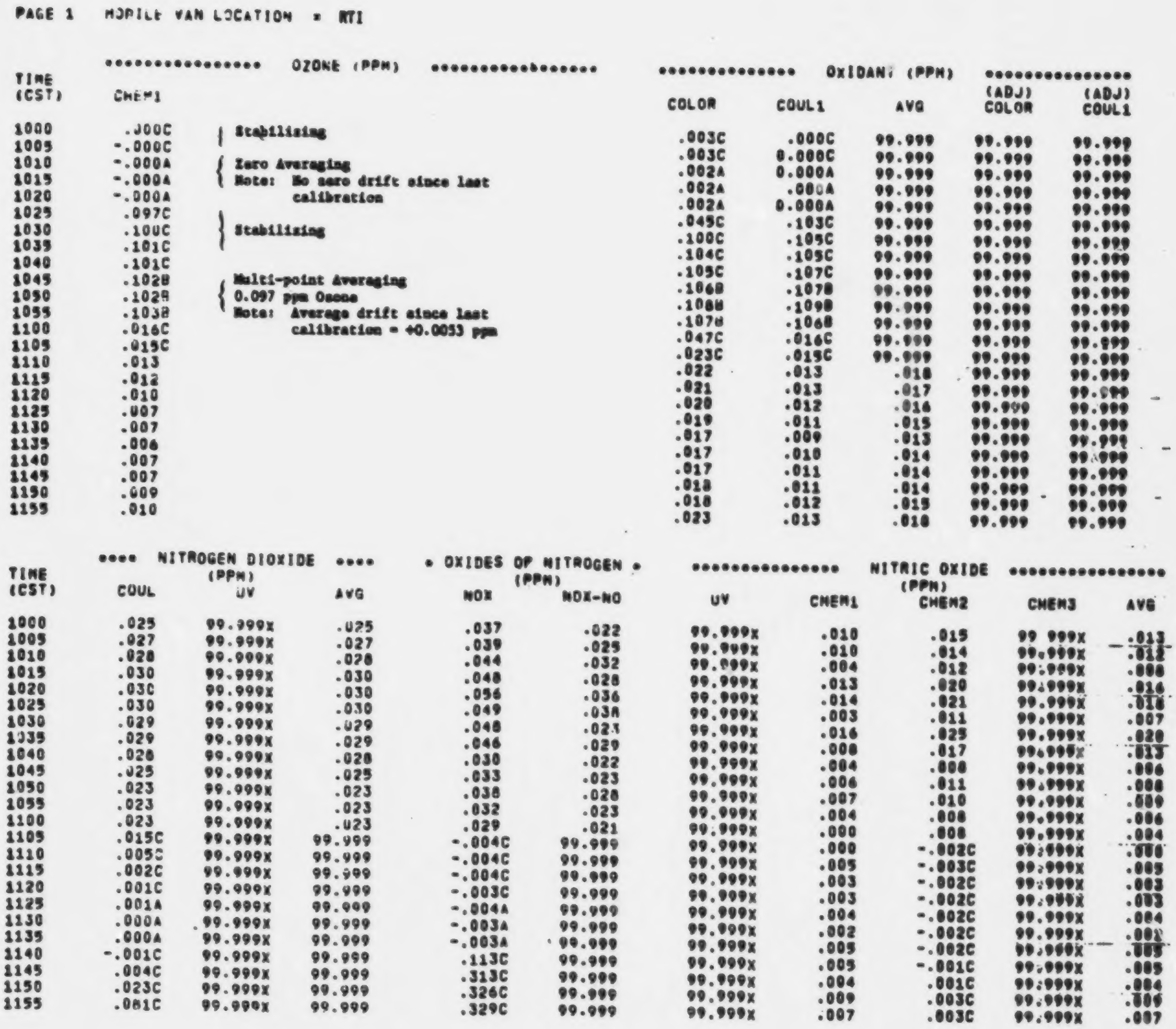


Figure 2.4: Automatic Calibration Procedure Showing Mode Switch Settings



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PAGE 1   MOBILE VAN LOCATION  =  RTI

        ****************   OZONE (PPM)   ****************     **************   OXIDANT (PPM)   **************
TIME                                                                                            (ADJ)      (ADJ)
(CST)    CHEM1                                               COLOR      COUL1      AVG         COLOR      COUL1

1000      .000C   | Stabilizing                               .003C      .000C    99.999      99.999     99.999
1005     -.000C   |                                           .003C     0.000C    99.999      99.999     99.999
1010     -.000A  { Zero Averaging                             .002A     0.000A    99.999      99.999     99.999
1015     -.000A  { Note:  No zero drift since last            .002A      .000A    99.999      99.999     99.999
1020     -.000A            calibration                        .002A     0.000A    99.999      99.999     99.999
1025      .097C   }                                           .045C      .103C    99.999      99.999     99.999
1030      .100C   } Stabilizing                               .100C      .105C    99.999      99.999     99.999
1035      .101C   }                                           .104C      .105C    99.999      99.999     99.999
1040      .101C                                               .105C      .107C    99.999      99.999     99.999
1045      .102B  { Multi-point Averaging                      .106B      .107B    99.999      99.999     99.999
1050      .102B  { 0.097 ppm Ozone                            .108B      .109B    99.999      99.999     99.999
1055      .103B  { Note:  Average drift since last            .107B      .106B    99.999      99.999     99.999
1100      .016C            calibration = +0.0033 ppm          .047C      .016C    99.999      99.999     99.999
1105      .015C                                               .023C      .015C    99.999      99.999     99.999
1110      .013                                                .022       .013       .018      99.999     99.999
1115      .012                                                .021       .013       .017      99.999     99.999
1120      .010                                                .020       .012       .016      99.999     99.999
1125      .007                                                .019       .011       .015      99.999     99.999
1130      .007                                                .017       .009       .013      99.999     99.999
1135      .006                                                .017       .010       .014      99.999     99.999
1140      .007                                                .017       .011       .014      99.999     99.999
1145      .007                                                .018       .011       .014      99.999     99.999
1150      .009                                                .018       .012       .015      99.999     99.999
1155      .010                                                .023       .013       .018      99.999     99.999


        ****  NITROGEN DIOXIDE  ****     * OXIDES OF NITROGEN *     ****************   NITRIC OXIDE   ****************
TIME             (PPM)                          (PPM)                                      (PPM)
(CST)    COUL       UV         AVG         NOX        NOX-NO        UV         CHEM1       CHEM2       CHEM3       AVG

1000      .025    99.999X      .025        .037        .022       99.999X      .010        .015      99 999X      .013
1005      .027    99.999X      .027        .039        .025       99.999X      .010        .014      99.999X      .012
1010      .028    99.999X      .028        .044        .032       99.999X      .004        .012      99.999X      .008
1015      .030    99.999X      .030        .048        .028       99.999X      .013        .020      99.999X      .016
1020      .030    99.999X      .030        .056        .036       99.999X      .014        .021      99.999X      .018
1025      .030    99.999X      .030        .049        .038       99.999X      .003        .011      99.999X      .007
1030      .029    99.999X      .029        .048        .023       99.999X      .016        .025      99.999X      .020
1035      .029    99.999X      .029        .046        .029       99.999X      .008        .017      99.999X      .013
1040      .028    99.999X      .028        .030        .022       99.999X      .004        .008      99.999X      .006
1045      .025    99.999X      .025        .033        .023       99.999X      .006        .011      99.999X      .008
1050      .023    99.999X      .023        .038        .028       99.999X      .007        .010      99.999X      .009
1055      .023    99.999X      .023        .032        .023       99.999X      .004        .008      99.999X      .006
1100      .023    99.999X      .023        .029        .021       99.999X      .000        .008      99.999X      .004
1105      .015C   99.999X    99.999       -.004C     99.999       99.999X      .000       -.002C     99.999X      .000
1110      .005C   99.999X    99.999       -.004C     99.999       99.999X      .005       -.003C     99.999X      .005
1115      .002C   99.999X    99.999       -.004C     99.999       99.999X      .003       -.002C     99.999X      .003
1120      .001C   99.999X    99.999       -.003C     99.999       99.999X      .003       -.002C     99.999X      .003
1125      .001A   99.999X    99.999       -.004A     99.999       99.999X      .004       -.002C     99.999X      .004
1130      .000A   99.999X    99.999       -.003A     99.999       99.999X      .002       -.002C     99.999X      .002
1135      .000A   99.999X    99.999       -.003A     99.999       99.999X      .005       -.002C     99.999X      .005
1140     -.001C   99.999X    99.999        .113C     99.999       99.999X      .005       -.001C     99.999X      .005
1145      .004C   99.999X    99.999        .313C     99.999       99.999X      .004        .001C     99.999X      .004
1150      .023C   99.999X    99.999        .326C     99.999       99.999X      .009        .003C     99.999X      .006
1155      .081C   99.999X    99.999        .329C     99.999       99.999X      .007        .003C     99.999X      .007
```

Figure 2.5: Automatic Calibration Printout

The computed concentrations are retained and printed out at the end of each hour along with the hourly average of the data for that instrument.

In addition to the output at the end of each hour, data may also be output after each five-minute scan if requested by the operator. This includes a list of:

(1) the voltages read by the data acquisition system,

(2) the concentrations computed, or

(3) the equations used to convert the voltage reading to a concentration.

The program was also designed to assist the operator in performing calibration procedures. It senses when an instrument is being calibrated by means of the analyzer mode switch status channel. The program then stores for each instrument in calibration (up to 10) all the valid calibration data points (i.e., the measured instrument output voltage and the corresponding calibration gas). Upon completion of the multipoint calibration as indicated by the appearance of the proper operational mode switch code in the instrument status channel, the calibration data points are fed into a regression subroutine; and a least-squares, best-fit equation is automatically computed. This equation then replaces the one already in storage and is used to process data from that point on. Both the new and old regression equations can be printed out for comparison.

A flow chart of the program used in the evaluation program is presented in Figure 2.6 and consists basically of two loops. The outer loop is completed every five minutes (once for every scan of the data acquisition system). The inner loop is scanned once for each instrument every five minutes. Since it is a real-time program, it has no end but is intended to run until manually halted.

Program operation starts with an initialization phase in which elements of arrays are set to zero and data regarding system configuration are read in. Then the program enters the loop. Here the first step is to print out the system configuration data for checking and editing, if any exist. Then the voltages are read from the data acquisition system and stored along with the time of the reading. This reading can occur only during a scan,

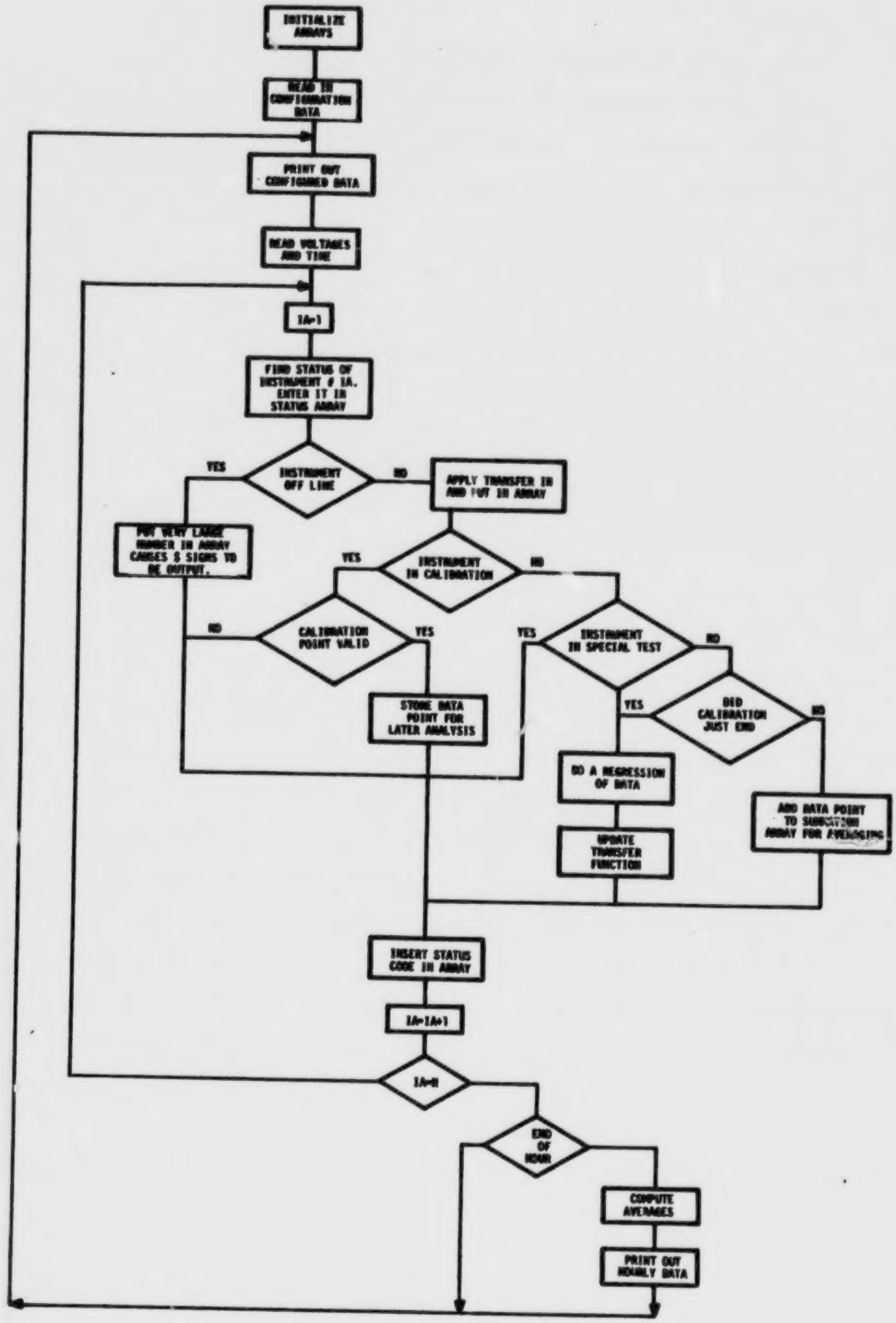

INITIALIZE ARRAYS
READ IN CONFIGURATION DATA
PRINT OUT CONFIGURED DATA
READ VOLTAGES AND TIME
IA=1
FIND STATUS OF INSTRUMENT # IA. ENTER IT IN STATUS ARRAY
YES
INSTRUMENT OFF LINE
NO
APPLY TRANSFER IN AND PUT IN ARRAY
PUT VERY LARGE NUMBER IN ARRAY CAUSES $ SIGNS TO BE OUTPUT.
YES
INSTRUMENT IN CALIBRATION
NO
NO
CALIBRATION POINT VALID
YES
YES
INSTRUMENT IN SPECIAL TEST
NO
STORE DATA POINT FOR LATER ANALYSIS
YES
DID CALIBRATION JUST END
NO
DO A REGRESSION OF DATA
UPDATE TRANSFER FUNCTION
ADD DATA POINT TO SUBSTATION ARRAY FOR AVERAGING
INSERT STATUS CODE IN ARRAY
IA=IA+1
IA=N
END OF HOUR
COMPUTE AVERAGES
PRINT OUT HOURLY DATA

Figure 2.6: Program Flow Chart

and since the hardware is set only to scan once every five minutes, the voltages are read every five minutes also. The program then enters the inner loop where the individual instrument voltages are picked from the voltage list for each instrument. First, from the array which contains the data on how the system is configured, two numbers are obtained:

(1) the channel number of the data for that instrument, and

(2) the channel number of the status line for that instrument.

The program then enters a decision phase to determine what to do with the data. This is accomplished by examining the individual instrument status channel. The voltage on the status channel, which normally ranges from 0-1 volt, is multiplied by 10 and rounded off to the nearest integer. The value of this integer is tested to see what to do with the data point. If the instrument was off line for any of the reasons coded on the status switch, an excessively large number is entered in the slot in a 20 x 12 array corresponding to 20 instrument readings (to be in $\mu g/m^3$) by 12 scans/hour. This will cause $$$ to be printed out when this array is listed at the end of the hour. Also, the appropriate letter code is inserted in the status array to indicate the reason why the instrument was off line.

If the instrument was being calibrated, the data must be treated differently. First, the actual concentration is computed and entered in the DATA array and the code for either calibration, stabilization or calibration data point is entered in the STATUS array. If the calibration point was a valid point, another step must be taken as well. The voltage measured and the standard value obtained from the operator are entered in the appropriate array. Only two possibilities remain for the status. The first is a special test for which no action is taken other than putting computed data points in the DATA array and the appropriate Literal in the STATUS array. The last possible status choice, measure, is the most often used. This means a valid data point resulting from a measurement of ambient air. For this data point the computed value is entered in the data array, a blank entered in the STATUS array, and the value is added to a summation location for computing an hourly average at the end of the hour.

Also a test is made to see if this is the first data point after a calibration; if so, the set of calibration data is fed to a regression subroutine for the computation of the calibration equation. The new equation then replaces the old and both are output.

This procedure is repeated for all instruments after each data scan until the end of the hour. At this time a summary of all data points is printed out along with the computed hourly averages. The DATA and STATUS arrays are then reinitialized, and the program starts over. A typical example of a five-minute, long-form data printout with regression analysis and updated transfer equation is shown in Figure 2.7, and an hourly average summary printout is shown in Figure 2.8.

```
   NOVEMBER 12, 1973         10:25 HOURS
  ┌ -.985  -.106  -.199  -.100   .000    .000  1.339    .000    .000  -.000
  │  .013   .019   .000  -.061   .000  15.028-15.054  -.000  -.002   .000
  │ -.019   .186   .239   .023   .011  -.037  -.002  -.053   .000  2.540
 1│ 4.583   .030   .023   .010  -.038  -.012   .027   .011   .005  -.008
  │  .000  -.000  -.001  -.001  -.000  -.990  -.106  -.512  -.512  -.107
  │ -.608  -.608  -.512  -.608  -.106  -.106  -.984  -.106-13.226-13.198
  └-13.196-13.176-13.175-13.181-13.176
  ┌REGRESSION ANALYSIS COMPLETE FOR BEK THC
  │OLD COEF.  Y=  654.87756 *X +    .00100
  │NEW COEF.  Y=  656,99023 *X +   -.00439
 2│REGRESSION ANALYSIS COMPLETE FOR BEK CH4
  │OLD COEF.  Y=  646.25708 *X +   -.01950
  └NEW COEF.  Y=  658.65808 *X +   2.07227
  ┌RTI 03         4.6158       UG/M
  │BEN 03        74.2662       UG/M
  │BEN NO     $$$$$$$$$$ X     UG/M
  │BEN NO2    $$$$$$$$$$ X     UG/M
  │BEN TS     $$$$$$$$$$ X     UG/M
  │BEK THC     1663.3247       UG/M
 3│BEK CH4     2961.5825       UG/M
  │BEK CO     $$$$$$$$$$ M     UG/M
  │BEN 03        73.2735       UG/M
  │BEN THC     1223.5066 T     UG/M
  │BEN CH4     1568.9365 T     UG/M
  └BEN NMHC    -335.2686 T     UG/M
```

1 - Output from each channel in mV, reading from left to right

2 - Transfer equation data obtained from current and prior calibration

3 - Selected channels and values computed and stored

Figure 2.7: Data Available on 5-min Interval

```
R.T.I. STUDY

JANUARY 23, 1973

         BEN TS     BEK THC  BEK CH4   BEK CO      BEN 03
TIME      UG/M        UG/M     UG/M     UG/M        UG/M
 13 0     134.T       1200.     780.     162.     $$$$$$$M
 13 5     132.T       1196.     787.     252.     $$$$$$$M
 1310     131.T       1165.     787.     227.     $$$$$$$M
 1315     131.T       1203.     794.     224.     $$$$$$$M
 1320     132.T       1194.     772.     107.     $$$$$$$M
 1325     131.T       1186.     779.     269.     $$$$$$$M
 1330     132.T       1166.     790.     234.     $$$$$$$M
 1335     133.T       1166.     786.     188.     $$$$$$$M
 1340        .C       1183.     780.     162.     $$$$$$$M
 1345        .C       1174.     786.     217.     $$$$$$$M
 1350        .C       1156.     793.     204.     $$$$$$$M
 1355        .C       1188.     790.     172.     $$$$$$$M

AVERAGE $$$$$$$       1181.     785.     202.     $$$$$$$
```

Code for Status of
Instrument (Blank for
Ambient Air Data Point)

$$$ - Indicates Less than
9 Valid Data Points During
Past Hour, Hence No Average
is Computed

Figure 2.8: Hourly Average Summary Printout

3.0 SELECTION OF INSTRUMENTS

3.1 SELECTION CRITERIA

Operational requirements, definitions describing sensor specifications, and sensor specifications applicable to the special needs of the RAPS Program were prescribed in the section of RFP-DU-73-A016 describing instrumentation and are presented in Table 3.1. These specifications and requirements provided the basic criteria for selection of analyzers and are as follows: (1) accuracy, (2) maximum reliability, and (3) long-term unattended operation. Other factors considered important in the selection process were commercial availability, prior evaluation, proven field reliability, and accessibility. It was readily apparent from the onset of the program that all available brand name models of chemiluminescent ozone monitors, for instance, could not be included in the evaluation program due to monetary and time constraints. Therefore, subjective judgment was utilized to choose a particular model for evaluation to determine if the measurement principle, as represented by that particular model, could meet the specifications required for the RAPS Program. Much consideration was given to all available manufacturers of instrumentation within each category prior to selection of an instrument or instruments for that category. All available results obtained from previous instrument evaluation programs were utilized in the selection process. In the case of ozone instrumentation one instrument was considered adequate to conduct the evaluation; while for the other pollutants numerous analyzers available at the time of the evaluation were considered and tested. For example, several chemiluminescent NO_2 analyzers were tested. This judgment was based on prior knowledge of proven field reliability of the measurement principle and, to some extent on the reliability of the instrument chosen for the evaluation. This should not be interpreted to mean, however, that other instruments not included in the evaluation program within each category would not or could not meet the required specifications. The instrumentation and measurement methods evaluated in this program are summarized in Table 3.2. The principle of operation of these instruments and measurement methods are described in detail in Section 4.0.

Table 3.1. SENSOR SPECIFICATIONS

Parameter	Measurement Principle	Range (PPM)	Sensitivity (PPM)*	Accuracy/	Precision	Drift/Week Zero	Span	Operational Period (days)
H_2S	GC-Flame Photometry	0-0.1 0-1.0	0.002 0.010	±2%	±2%	±3%	±2%	14
SO_2	Flame Photometry	0-0.2 0-1.0	0.005	±3%	±2%	±3%	±2%	14
O_3	Chemiluminescence	0-0.2	0.005	±5%	±2%	±5%	±4%	14
NO/NO_2	Chemiluminescence	0-0.5 0-2.0	0.005 0.020	±5%	±2%	±5%	±4%	14
CO	GC-Flame Ionization	0-10, 0-25 0-50, 0-100	0.100	±2%	±2%	±3%	±2%	30
THC/CH_4	GC-Flame Ionization	0-10, 0-25	0.100	±2%	±2%	±3%	±2%	30
NMHC	GC-Flame Ionization	0-10	0.100	±2%	+2%	±3%	±2%	30

*To convert ppm to μg/m^3 at 25°C and 760 mmHg, multiply ppm × the following constants:

H_2S - 1391
SO_2 - 2618
O_3 - 1963
NO - 1227
NO_2 - 1880
CO - 1145
CH_4 - 654

TABLE 3.2. INSTRUMENTATION AND MEASUREMENT METHODS EVALUATED

Pollutant	Instrument	Principle of Operation
Ozone	Bendix Model 8002	Chemiluminescence
	Dasibi Model 1003-AH	UV-Absorption
Nitric Oxide/ Nitrogen Dioxide	Bendix Model 8101-B	Chemiluminescence
	Meloy Model 520	Chemiluminescence
	Thermo Electron Model 14	Chemiluminescence
	Rem Model 642	Chemiluminescence
Sulfur Dioxide	Bendix Model 8300	Flame Photometry
	Meloy Model SA-185R	Flame Photometry
Hydrocarbons	Beckman Model 6800	GC-Flame Ionization
	Bendix Model 8201	GC-Flame Ionization
Carbon Monoxide	Beckman Model 6800	GC-Flame Ionization
	Andros Model 7000	DI-Fluorescence
	Bendix Model 8501-5FA	Non-Dispersive Infrared
Total Sulfur/Hydrogen Sulfide/Sulfur Dioxide	Tracor Model 270-HA	GC-Flame Photometry
	Bendix Model 8700	GC-Flame Photometry

3.2 TEST PLAN

Operational requirements expressed in the specifications for each sensor refer to the characteristics of the sensor as a unit from the inlet sample port of the instrument to the actual output of the sensor. The original test plan for the evaluation program is presented in Figure 3.1 and was divided into two parts. Briefly, Part I of the test plan was concerned with identification of critical points in the measurement process and the sensor's ability to meet the specifications presented in Table 3.1, Section 3.1. Test procedures described in detail in Section 5.0 and computer programming techniques developed during the performance of Contract CPA 70-101, "Field Evaluation of New Air Pollution Monitoring Systems," were utilized to determine the following performance characteristics for each sensor: lag, rise and fall time, sensitivity, precision, zero and span drift, linearity, operational period, etc. Part II of the evaluation program involved recommendations of engineering modifications to correct deficiencies if a given sensor failed to meet any specification.

Outputs of the test plan considered important were documentation of performance characteristics; modification, if necessary, of sensor to improve performance; retesting of sensor after modification to determine compliance with specifications; and rejection of sensor and/or documentation of performance characteristics if sensor met all requirements. Early identification of weaknesses or problems was considered imperative to accomplish the program objectives. To do this required the use of on-line data processing in quasi-real time. This feature of the evaluation program was accomplished via the use of an on-line computer. Another important facet of this program was to document in detail all modifications and/or recommendations to EPA or the manufacturer of a particular instrument to improve performance.

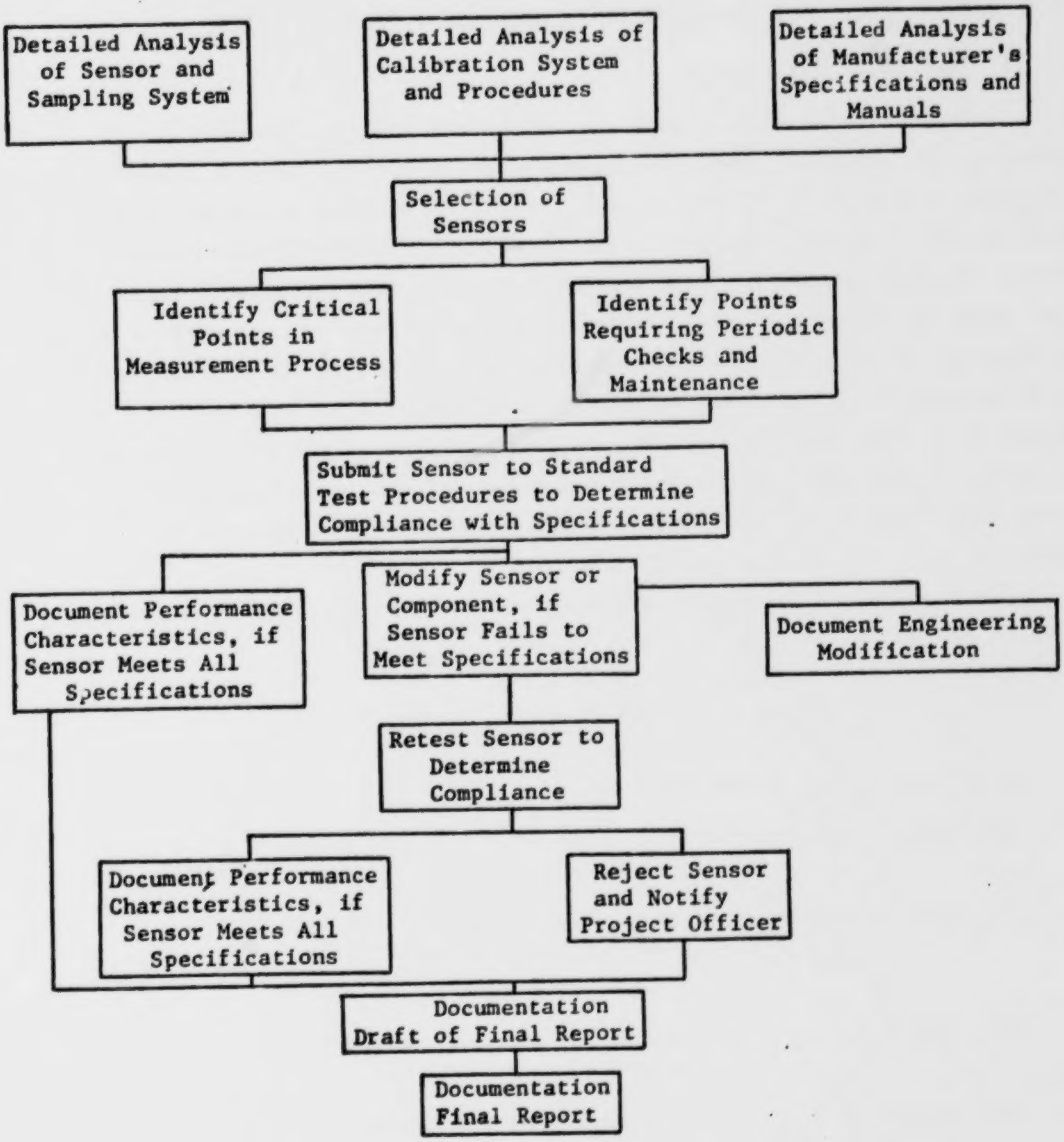

Detailed Analysis of Sensor and Sampling System
Detailed Analysis of Calibration System and Procedures
Detailed Analysis of Manufacturer's Specifications and Manuals
Selection of Sensors
Identify Critical Points in Measurement Process
Identify Points Requiring Periodic Checks and Maintenance
Submit Sensor to Standard Test Procedures to Determine Compliance with Specifications
Document Performance Characteristics, if Sensor Meets All Specifications
Modify Sensor or Component, if Sensor Fails to Meet Specifications
Document Engineering Modification
Retest Sensor to Determine Compliance
Document Performance Characteristics, if Sensor Meets All Specifications
Reject Sensor and Notify Project Officer
Documentation Draft of Final Report
Documentation Final Report

Figure 3.1: Test Plan Flowchart

4.0 GAS ANALYZERS

4.1 BENDIX MODEL 8002 GAS PHASE CHEMILUMINESCENT OZONE ANALYZER

4.1.1 Instrument Description

The theory of operation of the Bendix Model 8002 ozone analyzer is based on the gas phase chemiluminescent reaction of ozone with ethylene[5]. Ozonized or sample air (1 ℓ/min) and ethylene (25 cc/min) are mixed in a shallow cavity closely coupled to the cathode face of a photomultiplier tube. The photomultiplier tube current resulting from the detection of the chemiluminescence of the flameless reaction of ethylene gas with ozone is directly proportional to the concentration of ozone in the air sample. A block diagram of the chemiluminescent ozone analyzer is shown in Figure 4.1. The ethylene reaction has been reported in the literature to be specific for ozone, and no known components of the lower troposphere other than ozone have been observed to give chemiluminescence with the reactive gas[6].

The physical characteristics and other descriptors of the Bendix ozone monitor are as follows:

(1) overall dimensions: 16.5 in (42 cm) width,
8.5 in (2.15 cm) height,
18.5 in (47 cm) depth;

(2) weight: 45 pounds (20.4 Kg)

(3) power requirements: 350 watts at 105 to 125 volts, 60 Hz;

(4) measurement ranges: 0.01, 0.02, 0.05, 0.1, 0.2, 0.5, and 1.0 ppm full scale (19.60-1960 μg/m^3);

(5) mode selector: ambient, zero, internal calibrate (fixed ozone concentration)

(6) adjustments: zero and span adjust potentiometers;

(7) outputs: 0-10 mV recorder; 0-1 VDC

(8) stated performance specifications (manufacturer)

  (a) minimum detectable sensitivity: 0.001 ppm (1.96 μg/m^3);

  (b) linearity: ± 0.5%;

  (c) noise: ± 1% on 0 to 0.1 ppm (0-196 μg/m^3) range;

  (d) measurement repeatability: ± 2% from mean value on the 0-0.1 ppm (0-196 μg/m^3) range;

  (e) accuracy: not specified

  (f) zero drift: ± 1% per day, ± 2% per three days

  (g) span drift: ± 1% per day, ± 2% per three days

  (h) operational period: 7 days or more unattended.

(9) required accessories: cylinder of ethylene gas, two-stage regulator, stripchart recorder

The gas flow system of the Bendix analyzer is composed of two parts, ethylene flow and sample flow. A flow diagram of the system is shown in Figure 4.2. Ethylene is provided by an external cylinder and two-stage regulator, and the ethylene flow rate is maintained by a pressure regulator and capillary designed to give a particular flow at a specified input pressure. A solenoid valve is provided for safety and is designed to shut off ethylene flow whenever AC-line voltage to the instrument is interrupted. Sample flow rate is maintained by a vacuum pump, needle valve, and flow meter arrangement. The needle valve is used to adjust the flow rate from the reaction chamber, and the flow meter is utilized to monitor this rate. Particulates greater than 5 microns in diameter are removed from the ambient air sample via a Teflon filter and prevented from entering the reaction chamber.

The detector cell of the analyzer consists of a reaction chamber located within the end plate block of the detector cell and a photomultiplier assembly. The assembly consists of a photomultiplier tube,

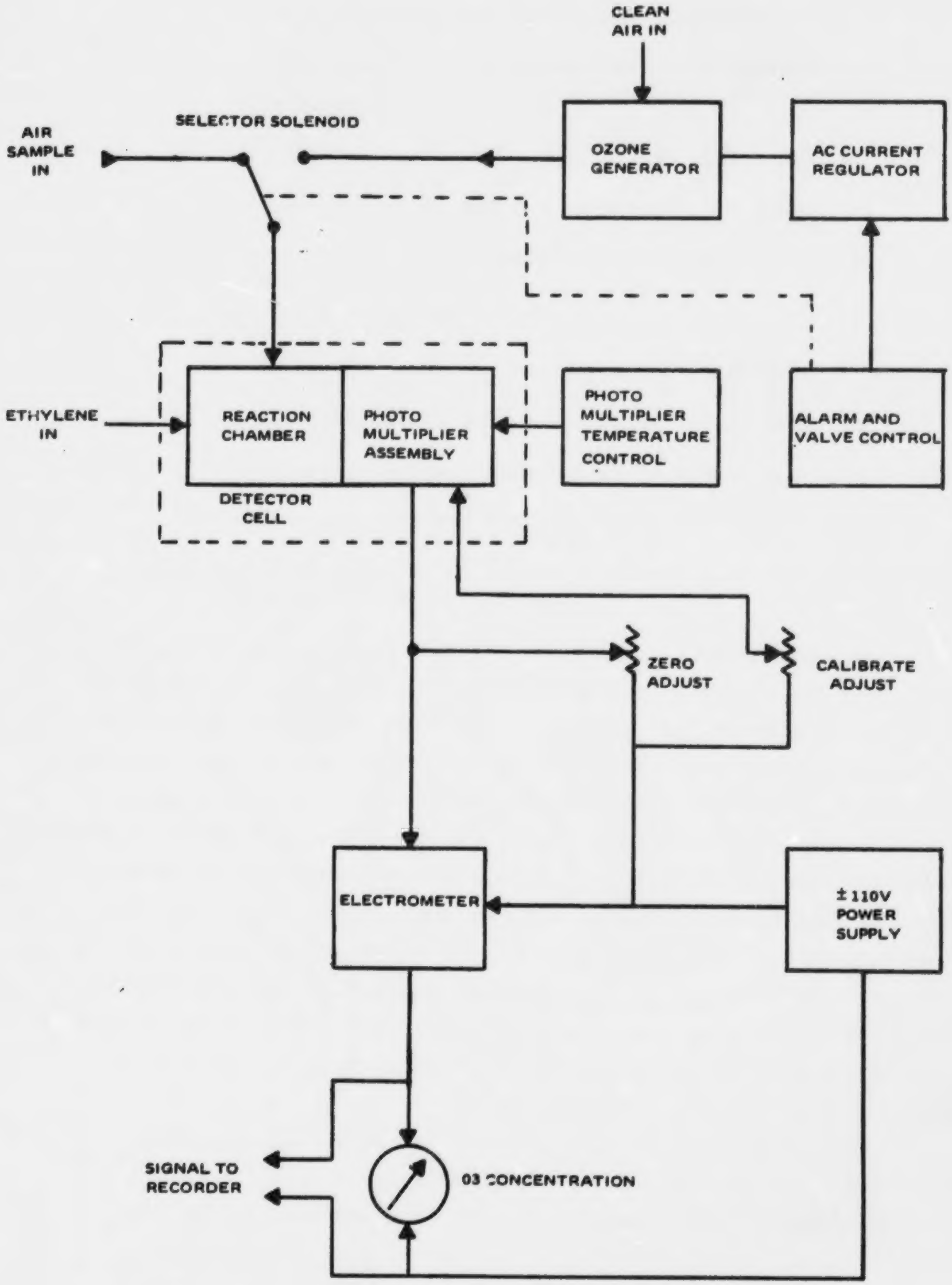

CLEAN AIR IN
AIR SAMPLE IN
SELECTOR SOLENOID
OZONE GENERATOR
AC CURRENT REGULATOR
ETHYLENE IN
REACTION CHAMBER
PHOTO MULTIPLIER ASSEMBLY
DETECTOR CELL
PHOTO MULTIPLIER TEMPERATURE CONTROL
ALARM AND VALVE CONTROL
ZERO ADJUST
CALIBRATE ADJUST
ELECTROMETER
± 110V POWER SUPPLY
SIGNAL TO RECORDER
03 CONCENTRATION

Figure 4.1: Ozone Monitor Simplified Block Diagram

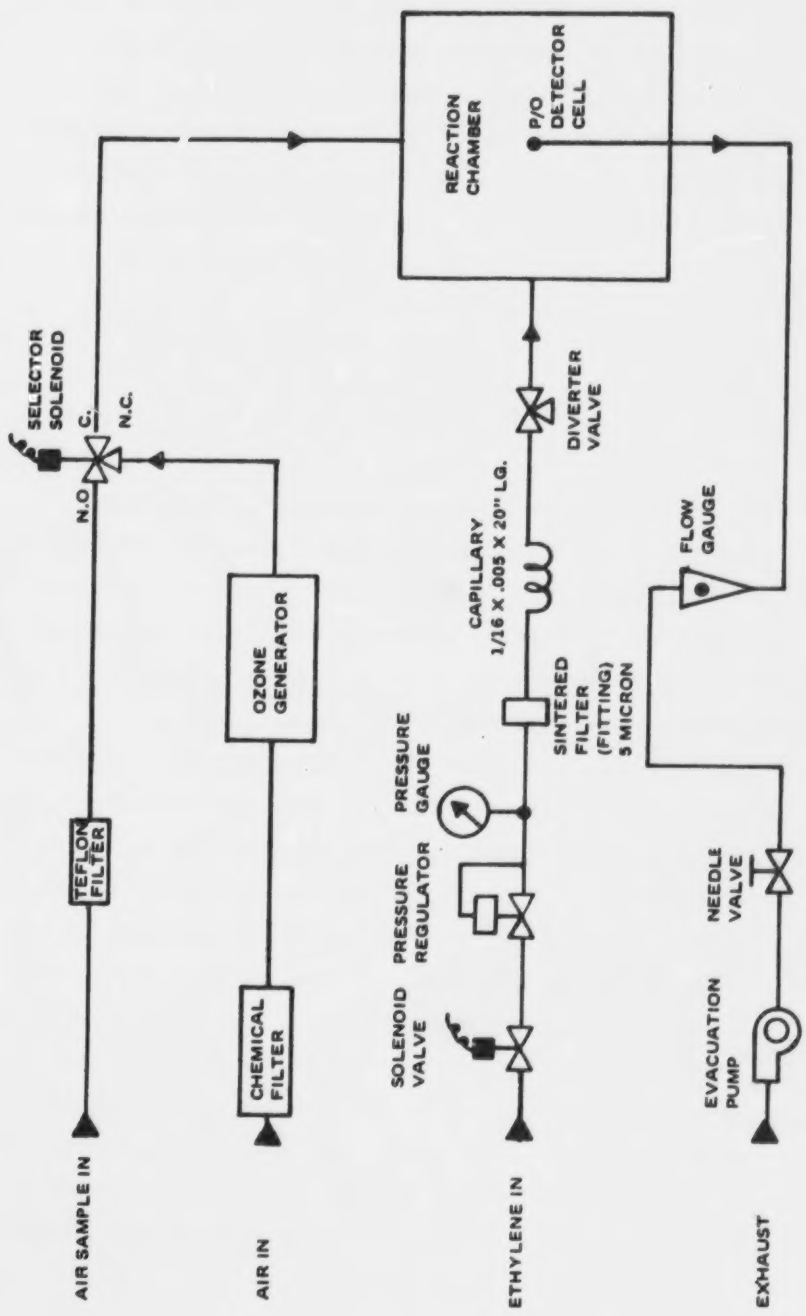

AIR SAMPLE IN
TEFLON FILTER
N.O.
SELECTOR SOLENOID
C.
N.C.
AIR IN
CHEMICAL FILTER
OZONE GENERATOR
REACTION CHAMBER
P/O DETECTOR CELL
ETHYLENE IN
SOLENOID VALVE
PRESSURE REGULATOR
PRESSURE GAUGE
SINTERED FILTER (FITTING) 5 MICRON
CAPILLARY 1/16 X .005 X 20" LG.
DIVERTER VALVE
EXHAUST
EVACUATION PUMP
NEEDLE VALVE
FLOW GAUGE

Figure 4.2: Ozone Monitor Flow Diagram

a high voltage power supply, thermoelectric coolers which maintain the cathode of the tube at 5°C, and a housing to enclose the three items. The basic function of the photomultiplier assembly is to convert the low-level photons resulting from the flameless reaction between ethylene and ozone to electrical energy and to amplify the electrical signal for further processing through the electrometer amplifier and recorder output/meter display circuitry. A schematic diagram of the detector cell is shown in Figure 4.3.

4.1.2 Operational Summary

The gas phase chemiluminescent analyzer was installed in the mobile van on December 18, 1972 and operated continuously until August 2, 1973. During this period of time both short-term and long-term tests were performed on the analyzer in accordance with the test plan requirements. The frequency of performance monitoring during these tests was dependent on the particular requirements of the evaluation procedure being applied. Calibration frequency for short-term drift was on a daily basis, and that for longer term drift studies was on a weekly or biweekly basis.

During the seven-month period in which the analyzer was operated and subjected to the performance evaluation tests, two failures occurred. The first failure involved the detector assembly and resulted from a power failure that lasted approximately two hours. Upon resumption of power, the analyzer failed to respond. The failure was attributed to failure of the detector power supply and required replacement of the detector cell. The other problem involved the inability of the analyzer to maintain a constant sample air-ethylene flow rate. This problem was traced finally to a baffle in the metal bellows vacuum pump and corrected. With the exception of these two problems, the analyzer required a minimum amount of maintenance. Routine maintenance involved replacement of the Teflon prefilter element on the sample inlet line on a monthly basis and replacement of the ethylene cylinder at six-month intervals.

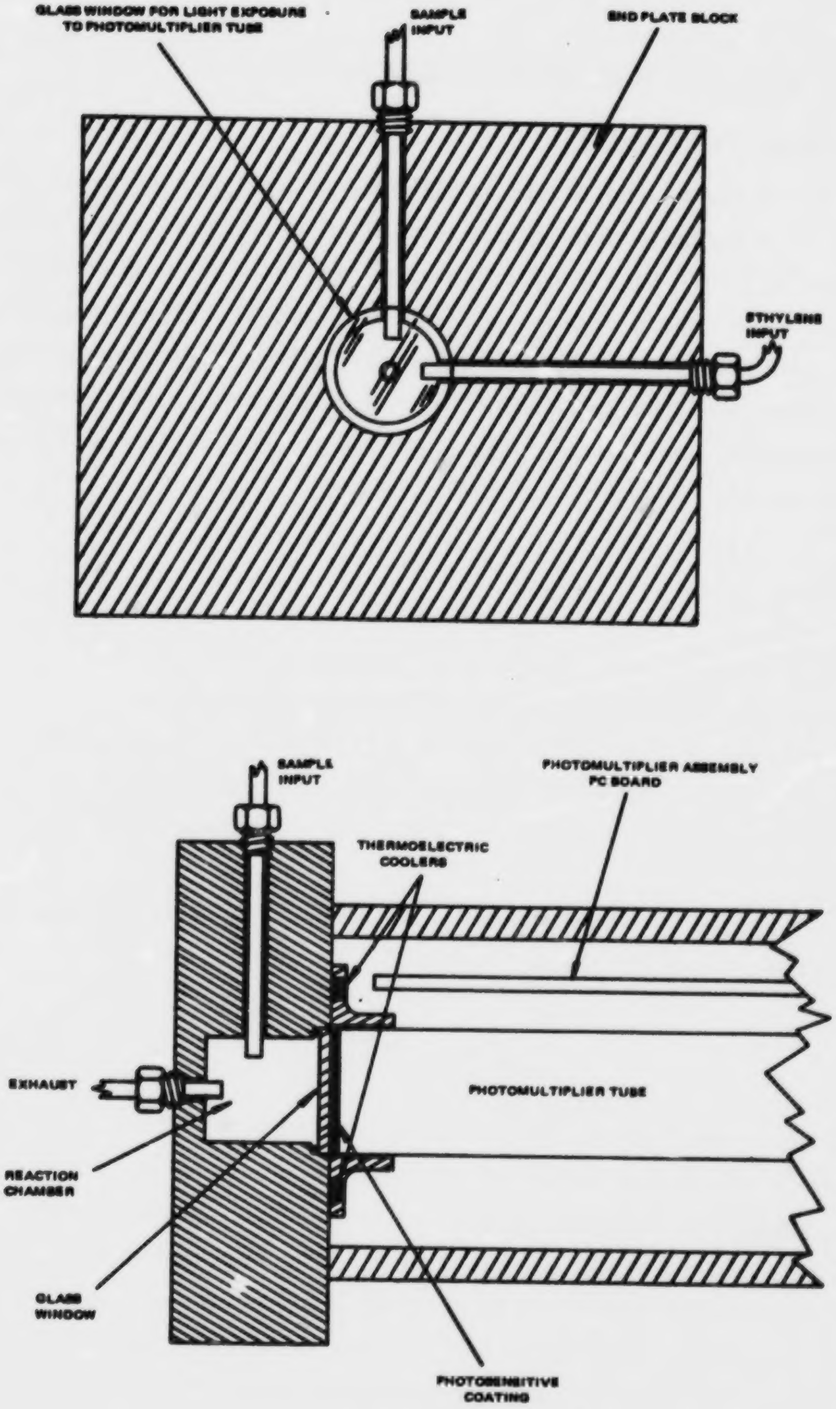

GLASS WINDOW FOR LIGHT EXPOSURE TO PHOTOMULTIPLIER TUBE
SAMPLE INPUT
END PLATE BLOCK
ETHYLENE INPUT
SAMPLE INPUT
PHOTOMULTIPLIER ASSEMBLY PC BOARD
THERMOELECTRIC COOLERS
EXHAUST
PHOTOMULTIPLIER TUBE
REACTION CHAMBER
GLASS WINDOW
PHOTOSENSITIVE COATING

Figure 4.3: Detector Cell

4.2 DASIBI MODEL 1003-AH ULTRAVIOLET OZONE ANALYZER

4.2.1 Instrument Description

The operation of the Dasibi Model 1003-AH analyzer is based upon the measurement of the absorption of ultraviolet (UV) light by ozone within a sample volume of air. Ultraviolet light is generated by a low-pressure mercury vapor lamp, which emits its strongest line at 2536.52 angstroms. This wavelength coincides with the region of maximum light absorption of ozone. By measurement of the amount of light absorbed by the sampled gas, the ozone concentration can be determined. The ozone concentration can be calculated from the following expression:

$$I_f/I_o = e^{-act}$$

where I_f = photocurrent of absorbed light,

I_o = photocurrent for zero concentration of ozone,

a = absorption coefficient = 2.74×10^{-4} cm^{-1},

c = concentration of ozone in ppm by volume, and

t = length of absorption chamber in centimeters.

The manner by which the above equation is mechanized in the Dasibi requires a variation of the expression as follows:

$$I_o - I_f = 1 - e^{-act} .$$

Basic components of the Dasibi analyzer are a gas flow system, UV source, sample chamber, absorption and reference detectors, digital electrometers, integration control logic and computation logic systems.

Figure 4.4 is a simplified block diagram of the Dasibi analyzer. Sample gas enters the inlet and is divided into two gas streams. A scrubber is utilized to remove ozone from the air sample in one line. Both sample and air minus ozone alternately enter the sample chamber through an electrically operated three-way solenoid valve. The absorption chamber has two windows

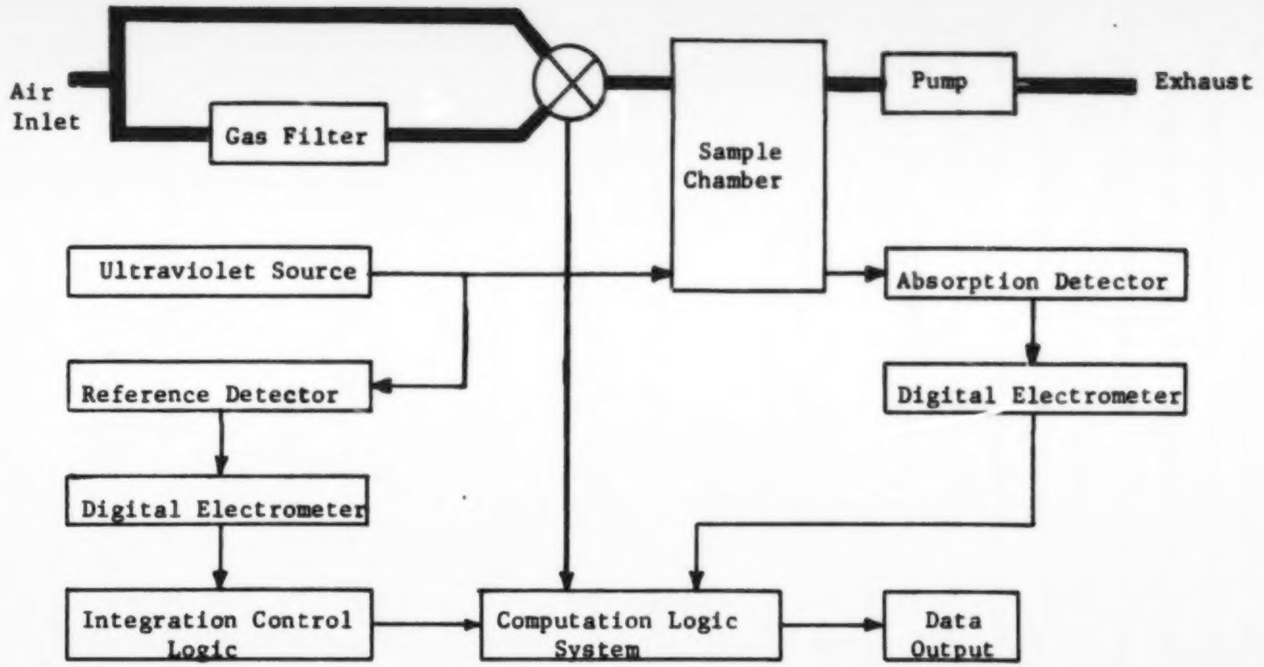

Air
Inlet
Gas Filter
Sample
Chamber
Pump
Exhaust
Ultraviolet Source
Absorption Detector
Reference Detector
Digital Electrometer
Digital Electrometer
Integration Control
Logic
Computation Logic
System
Data
Output

Figure 4.4: Schematic Diagram of UV Absorption Ozone Instrument

at opposite ends through which UV light passes, with the UV source being located at one end and the absorption detector at the other. Measurement begins when a signal from the electrically operated valve indicates that sample air minus ozone is flowing through the absorption chamber. At this time, the absorption detector starts to measure photons and integrates the result. At the same time the reference detectors starts counting to a preset value. The sequence is repeated again for the unfiltered gas. The difference between the integrated results for the filtered and unfiltered gas is computed and displayed digitally as the output concentration.

The physical characteristics and other descriptors of the Dasibi UV ozone analyzer are as follows:

(1) overall dimensions: 15 in (38.1 cm) width,
5.25 in (13.3 cm) height,
22 in (55.9 cm) depth;

(2) weight: 31 pounds (14.1 Kg);

(3) power requirements: 75 watts at 110 V, 60 Hz;

(4) measurement ranges: 0.003 to 20 ppm
(5.9 to 39200 $\mu g/m^3$);

(5) mode selectors: ambient, zero, calibrate;

(6) outputs:

(a) digital display - 0.003 to 20.0 ppm
(5.9 to 39,200 $\mu g/m^3$)

(b) analog - 0 - 0.999 V (Std)

(c) BCD (optional) - 8-4-2-1, Standard TTL;

(7) Stated performance specifications (manufacturer)

(a) minimum detectable sensitivity: 0.003 ppm
(5.9 $\mu g/m^3$);

(b) linearity: 1% (0.003 to 1.0 ppm)
(5.9 to 1960 $\mu g/m^3$);

(c) noise: not specified;

(d) precision ± 1%;

(e) accuracy: ± 3% (based on Beer's Law);

(f) zero drift: Digital and BCD output - (zero)
analog output - 0.5% per day;
1% per three days;

(g) span drift: Digital and BCD output - (zero)
analog output - 0.5% per day;
1% per three days;

(h) operational period: not specified;

(8) required accessories: none; stripchart recorder.

The gas flow system of the Dasibi analyzer is composed of two flow paths. Sample air flows through one flow path directly to the sample chamber and is alternately diverted through a scrubber which removes ozone from the sample stream. The time sequence is controlled by a timer, with switching occurring at 10 second intervals. Sample flow rate is maintained at approximately 2 liters per minute by a blower.

The absorption chamber consists of a folded tube approximately 0.4 inch (1.0 cm) in diameter and 30 inches (77 cm) in length with inlet and outlet gas ports. The chamber has two windows which are optically transparent at the 2537 Å emission. A solid-state photodiode detector is positioned adjacent to the outlet port and senses the UV radiation through the absorption chamber. At the light source end of the chamber, a second photodiode detector, which serves as a reference, senses the portion of light from the source. The electronic signals from the photodiode detectors are processed through the digital electrometers and computation logic systems.

4.2.2 Operational Summary

The Dasibi ozone analyzer was installed in the mobile van on July 12, 1973 and operated for a week's period of time. Due to time constraints and the unavailability of the analyzer from EPA for longer periods of time, a limited number of performance evaluation tests were performed. The major efforts were concerned with interference tests, minimum detectable concentration, and comparison of ambient data with that from a chemiluminescent ozone analyzer. No failures occurred during this period of time and no maintenance was required.

4.3 BENDIX MODEL 8101-B CHEMILUMINESCENT NO-NO_x-NO_2 ANALYZER

4.3.1 Instrument Description

The principle of operation of the Bendix Model 8101-B analyzer is based on the chemiluminescent gas phase reaction of nitric oxide (NO) and ozone (O_3)[7,8]:

$$NO + O_3 \longrightarrow NO_2^* + O_2$$

$$NO_2^* \longrightarrow NO_2 + h\nu.$$

Basic components of the analyzer are a reaction chamber, photomultiplier tube with a thermoelectric cooler, filter, electric discharge ozone generator, carbon-coated and heated converter, flow system, vacuum pump, electronic circuitry, and amplifier systems. Sample air (≈ 130 cc/min) and ozone (≈ 50 cc/min) are mixed prior to entering the reaction chamber which is closely coupled to the cathode face of a photomultiplier tube. Detection of the light emission from the reaction by the photomultiplier tube yields a signal with an amplitude proportional to the concentration of NO in the sample stream. The concentration of nitrogen dioxide (NO_2) in ambient air can be indirectly determined after quantitative conversion to nitric oxide by this chemiluminescent reaction. The NO concentration in the ambient air sample is first determined; then the sample air is diverted through a carbon converter (heated to 285°C) where NO_2 is reduced quantitatively to NO. The detector alternately measures NO and total oxides of nitrogen (NO + NO_2 reduced to NO) 30 seconds in each mode. By electronic subtraction of the amplitude of the NO signal from that of the NO_x signal, the concentration of NO_2 in the air sample is determined. Total time for the measurement cycle for the Bendix analyzer is one minute. Thus, 60 NO_2 measurement values are available for computing an hourly average. A block diagram of the chemiluminescent NO-NO_x-NO_2 analyzer is shown in Figure 4.5. Measurement of NO_2 via the chemiluminescent reaction of NO with O_3 is not subject to interference from any of the common air pollutants found in the ambient air, such as CO_2, CO, C_2H_4, NH_3, SO_2, and H_2O[9]; but recent evidence indicates a possible response to PAN (peroxy acetyl nitrate).

The physical characteristics and other descriptors of the Bendix NO-NO_x-NO_2 analyzer are as follows:

(1) overall dimensions: 16.5 in (42.0 cm) width;
8.5 in (21.5 cm) height; and
17 in (43.0 cm) depth;

(2) weight: 60 pounds (27.2 Kg);

(3) power requirements: 350 watts at 105 to 125 volts, 60 Hz;

(4) measurement ranges: 0.5, 1.0, 2.0, 5.0 ppm full scale (940-9400 μg/m^3);

(5) mode selectors: ambient, zero, span, NO mode only, NO_x mode only, NO-NO_2-NO_x mode;

(6) adjustment: zero and span adjustment potentiometers for NO, NO_x and NO_2 outputs;

(7) outputs: 0-10 mV recorder; 0-1 VDC;

(8) stated performance specifications (manufacturer)

  (a) minimum detectable sensitivity: 0.005 ppm (9.4 μg/m^3);

  (b) linearity: ± 0.5% full scale;

  (c) noise: 0.5% full scale;

  (d) precision: ± 0.01 ppm (18.8 μg/m^3) from 0.005 to 2.0 ppm (9.4-3760 μg/m^3) measured at integrator output;

  (e) accuracy: ± 0.01 ppm (18.8 μg/m^3) or ± 2% whichever is greater on the 0 to 2.0 ppm (0-3760 μg/m^3) scale;

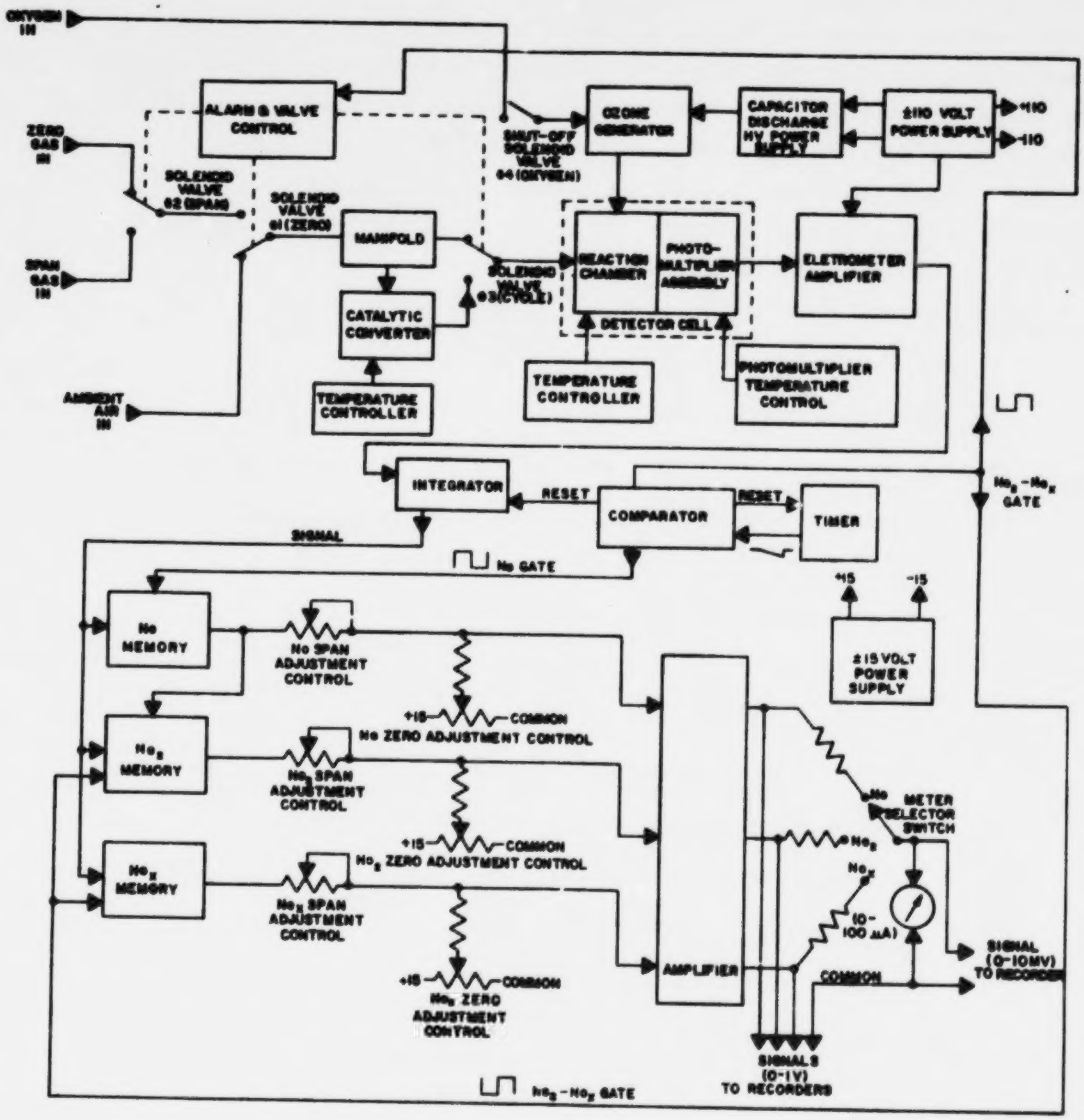

OXYGEN IN
ZERO GAS IN
SPAN GAS IN
AMBIENT AIR IN
ALARM & VALVE CONTROL
SOLENOID VALVE #2 (SPAN)
SOLENOID VALVE #1 (ZERO)
MANIFOLD
CATALYTIC CONVERTER
TEMPERATURE CONTROLLER
SOLENOID VALVE #3 (CYCLE)
SHUT-OFF SOLENOID VALVE #4 (OXYGEN)
OZONE GENERATOR
CAPACITOR DISCHARGE HV POWER SUPPLY
±110 VOLT POWER SUPPLY
+110
-110
REACTION CHAMBER
PHOTO-MULTIPLIER ASSEMBLY
DETECTOR CELL
ELETROMETER AMPLIFIER
TEMPERATURE CONTROLLER
PHOTOMULTIPLIER TEMPERATURE CONTROL
INTEGRATOR
RESET
COMPARATOR
RESET
TIMER
$No_2 - No_x$ GATE
SIGNAL
No GATE
+15
-15
±15 VOLT POWER SUPPLY
No MEMORY
No SPAN ADJUSTMENT CONTROL
+15
COMMON
No ZERO ADJUSTMENT CONTROL
No_2 MEMORY
No_2 SPAN ADJUSTMENT CONTROL
+15
COMMON
No_2 ZERO ADJUSTMENT CONTROL
No_x MEMORY
No_x SPAN ADJUSTMENT CONTROL
+15
COMMON
No_x ZERO ADJUSTMENT CONTROL
AMPLIFIER
No
METER SELECTOR SWITCH
No_2
No_x
(0-100 µA)
SIGNAL (0-10MV) TO RECORDER
COMMON
SIGNALS (0-1V) TO RECORDERS
$No_2 - No_x$ GATE

Figure 4.5: Oxides of Nitrogen Analyzer
Simplified Block Diagram

(f) zero drift: less than ± 1% per 24 hours;
less than ± 2% per 3 days;

(g) span drift: less than ± 2% per 24 hours;
less than ± 2% per 3 days;

(h) operational period: 7 days or more unattended;

(9) required accessories: cylinder of oxygen, two-stage regulator, stripchart recorder.

The gas flow system of the Bendix analyzer is composed of two parts (i.e., oxygen/ozone flow system and sample flow system). A flow diagram of the system is shown in Figure 4.6. The ozone generator used in this analyzer is a gas discharge type and produces approximately 1% of ozone at a flow rate of 50 cc/min of oxygen. Oxygen is provided by an external cylinder thru a two-stage regulator. The oxygen flow rate is maintained by use of a pressure regulator and capillary designed to give approximately 50 cc/min flow at a specified input pressure. A solenoid valve is provided for safety and designed to shut off oxygen flow anytime AC-line voltage to the instrument is interrupted. Sample flow rate is maintained at approximately 130-150 cc/min via use of a glass capillary which acts as a flow restrictor (critical orifice) and a two-stage diaphragm vacuum pump. Particulates greater than 5 microns in diameter are removed from the ambient air sample via a Teflon filter and prevented from entering the inlet lines and plugging the glass capillary.

The detector cell of the analyzer consists of a reaction chamber, optical filter, photomultiplier tube, high voltage power supply, thermoelectric coolers which maintain the cathode of the tube at 5°C, and a detector cell housing. The basic function of the photomultiplier assembly is to convert the low level photons resulting from the flameless reaction to electrical energy and amplify the electrical signal for further processing through the electrometer amplifier, integrator and memory circuitry. A schematic diagram of the detector cell is shown in Figures 4.7 and 4.8.

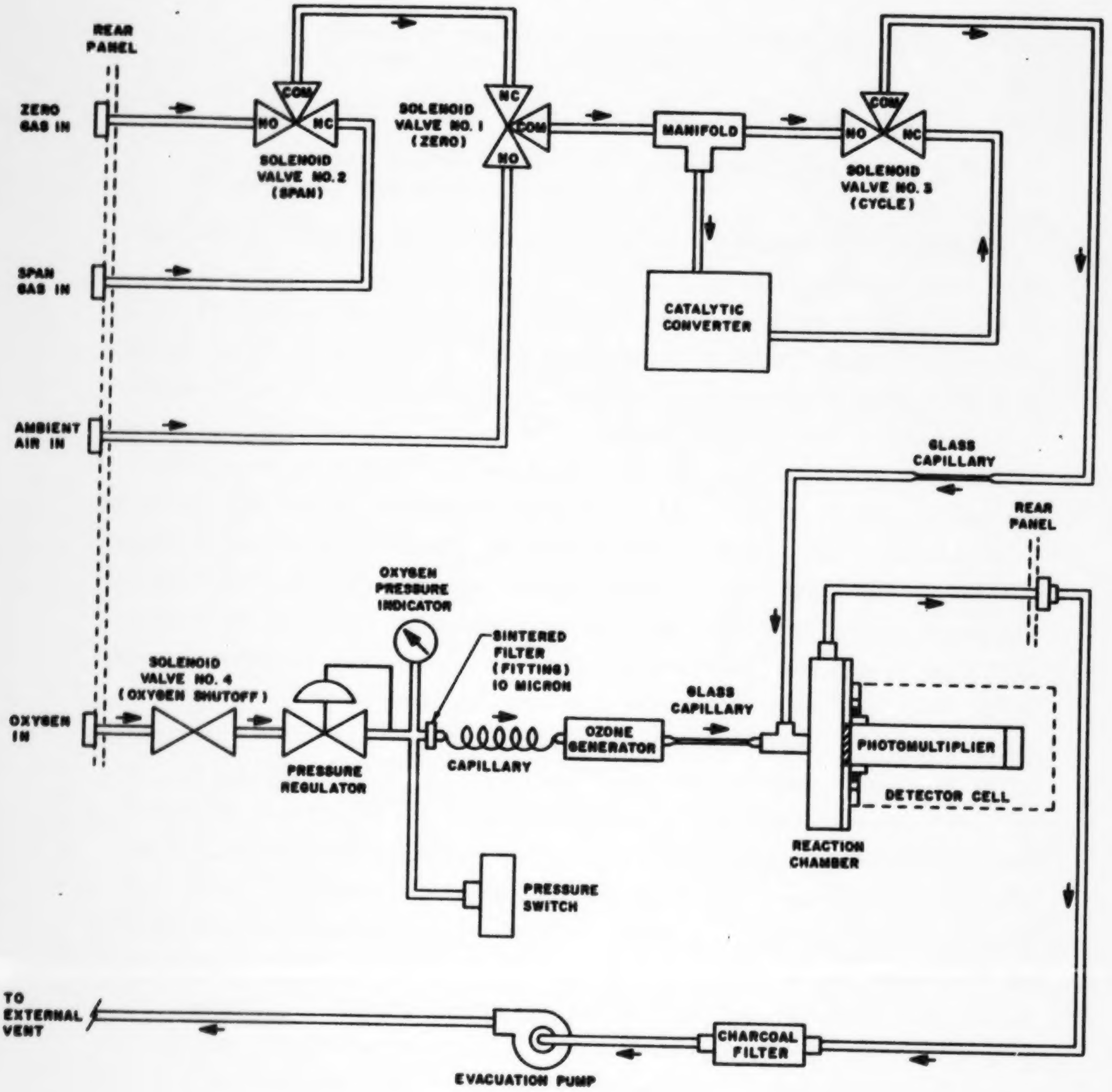

REAR PANEL
ZERO GAS IN
COM
NO
NC
SOLENOID VALVE NO. 2 (SPAN)
NC
COM
NO
SOLENOID VALVE NO. 1 (ZERO)
MANIFOLD
COM
NO
NC
SOLENOID VALVE NO. 3 (CYCLE)
SPAN GAS IN
CATALYTIC CONVERTER
AMBIENT AIR IN
GLASS CAPILLARY
REAR PANEL
OXYGEN PRESSURE INDICATOR
SINTERED FILTER (FITTING) 10 MICRON
SOLENOID VALVE NO. 4 (OXYGEN SHUTOFF)
OXYGEN IN
PRESSURE REGULATOR
CAPILLARY
OZONE GENERATOR
GLASS CAPILLARY
PHOTOMULTIPLIER
DETECTOR CELL
REACTION CHAMBER
PRESSURE SWITCH
TO EXTERNAL VENT
EVACUATION PUMP
CHARCOAL FILTER

Figure 4.6: Oxides of Nitrogen Analyzer Flow Diagram

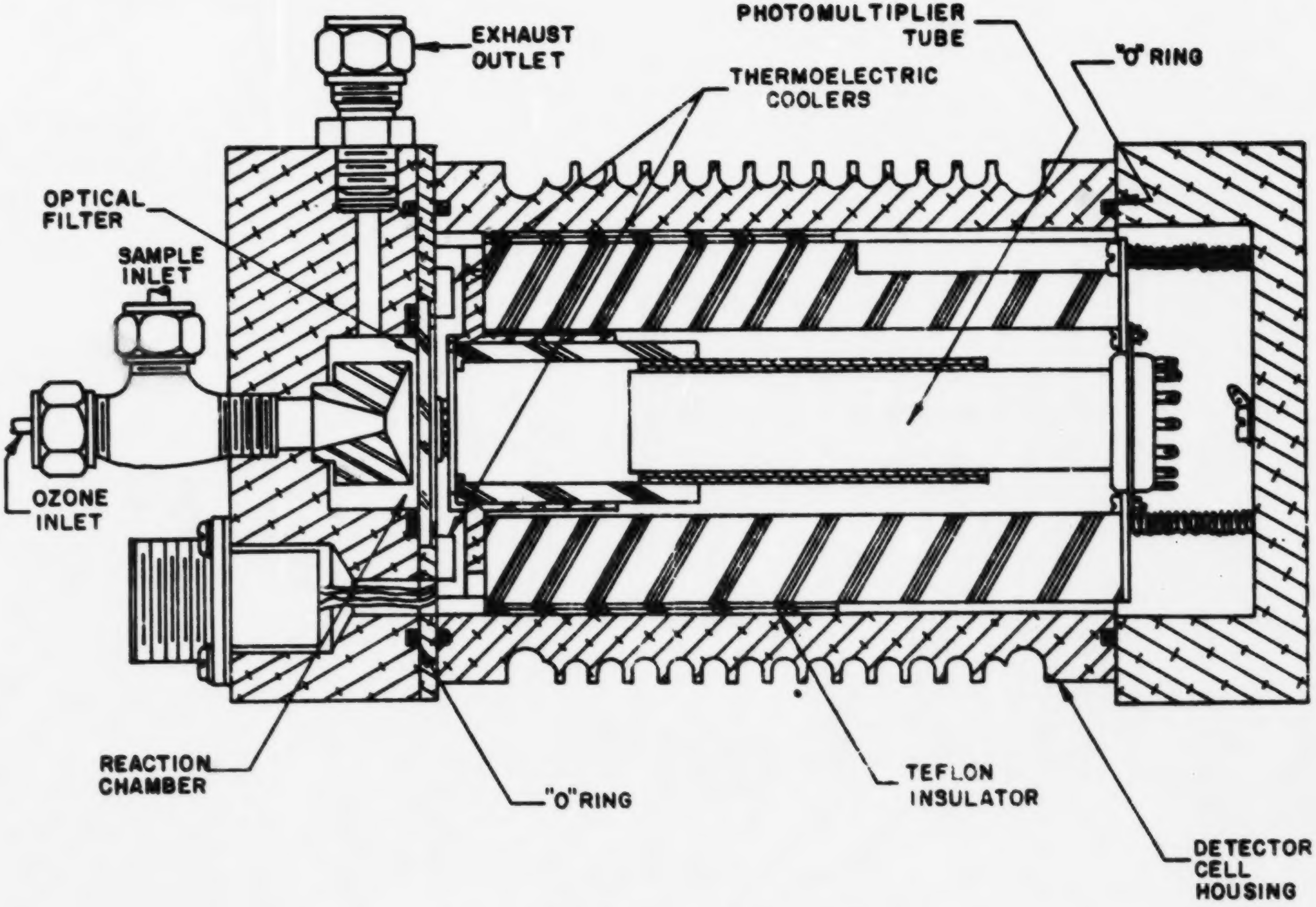

PHOTOMULTIPLIER TUBE
EXHAUST OUTLET
"O" RING
THERMOELECTRIC COOLERS
OPTICAL FILTER
SAMPLE INLET
OZONE INLET
REACTION CHAMBER
"O" RING
TEFLON INSULATOR
DETECTOR CELL HOUSING

Figure 4.7: Detector Cell Diagram

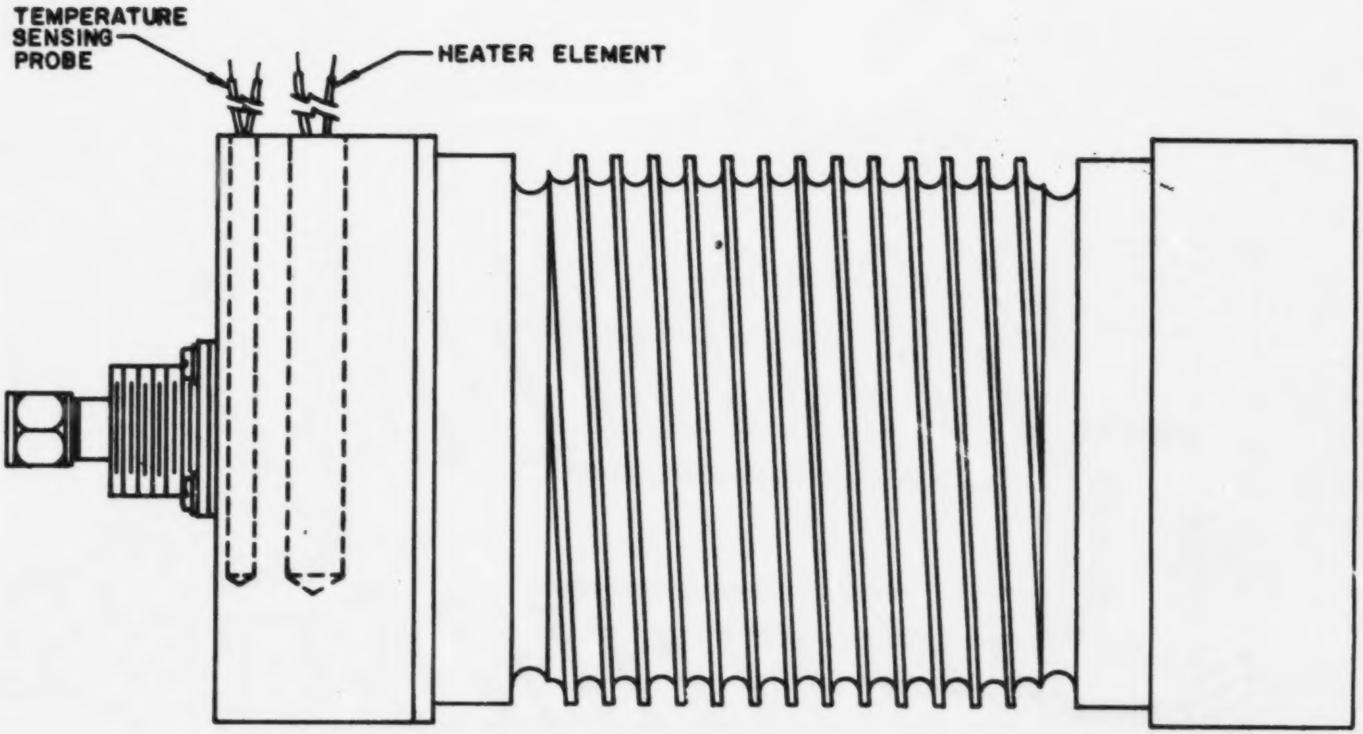

TEMPERATURE
SENSING
PROBE
HEATER ELEMENT

Figure 4.8: Detector Cell Housing

The catalytic converter used in the Bendix analyzer to reduce NO_2 to NO contains two tubes filled with ultra pure carbon. The catalyst block is heated to a temperature of 285°C to control the efficiency of the conversion process. Conversion efficiency of 98% has been reported.

4.3.2 Operational Summary

The chemiluminescent analyzer was installed in the mobile van on January 19, 1973 and operated continuously until June 13, 1973. During this period of time both short-term and long-term tests were performed on the analyzer in accordance with the test plan requirements. The frequency of performance monitoring during these tests was dependent on the particular requirements of the evaluation procedure being applied. Calibration frequency for short-term drift was on a daily basis, while for longer term drift studies the calibration frequency was on a weekly or biweekly basis.

During the six month period in which the analyzer was operated and subjected to the performance evaluation tests, two failures occurred. Both failures involved the two stage vacuum pumps used to maintain cell pressure within certain limits (i.e., $p < 7$ inches (17.8 cm) absolute pressure) and the proper flow rate at approximately 130-150 cc/min through the instrument. The response of the Bendix analyzer has been shown to be highly dependent on cell pressure with a minimum vacuum of 58.5 cm of Hg required for proper operation. Minor changes in the cell pressure will affect both the sensitivity of the measurement and calibration. Documentation of these results are presented in Section 7.0. A minimum amount of maintenance was required during this period of time. Routine maintenance involved replacement of the Teflon prefilter element on the sample inlet line and cleaning the residue from the ozonator electrode on a monthly basis. Accumulation or buildup of residue on the ozonator electrode contributed to propagation of radio frequency interference which adversely affects the operation of the memory and signal processing circuitry. Adequate shielding would have eliminated this effect.

4.4 MELOY MODEL 520 CHEMILUMINESCENT NO-NO_x-NO_2 ANALYZER

4.4.1 Instrument Description

Operation of the Meloy NO-NO_x-NO_2 analyzer is based on the flameless chemiluminescent reaction between NO and O_3:

$$NO + O_3 \rightarrow NO_2^* + O_2 \rightarrow NO_2 + h\nu \ .$$

The intensity of the radiation of the electronically excited NO_2^* molecules as they revert to lower energy states is directly proportional to the concentration of NO molecules involved in the reaction.

Basic components of the analyzer are a pneumatic sampling system, catalytic converter, high-voltage ozone generator, detector-chopper unit, flow controller, and associated electronics. Sample air and ozone (≈ 1000–3500 ppm) are mixed and chemically react within the detector chamber, which is coupled to the cathode face of a photomultiplier tube. Detection of the light emission from the reaction yields a signal whose amplitude is proportional to the concentration of NO in the sample stream. The concentration of NO_2 in the ambient air sample is then determined after quantitative conversion to NO, when the sample air is diverted through a catalytic converter. The detector alternately measures NO and total oxides of nitrogen (NO + NO_2 reduced to NO), 30 seconds in each mode. By electronic subtraction of the NO signal from the NO_x signal, the concentration of NO_2 in the air sample is determined. Total time for the measurement cycle is one minute. A block diagram of the chemiluminescent NO-NO_x-NO_2 analyzer is shown in Figure 4.9. Measurement of NO_2 via the reaction of NO with O_3 is not subject to interference from any of the common air pollutants in ambient air, such as CO_2, CO, C_2H_4, NH_3, SO_2, and H_2O[9]; but recent evidence indicates a possible response to PAN (peroxy acetyl nitrate).

The physical characteristics and other descriptors of the Meloy NO-NO_x-NO_2 analyzer are as follows:

(a) overall dimensions: 17 in (43 cm) width,
12.5 in (31.8 cm) height,
20.75 in (52.7 cm) depth;

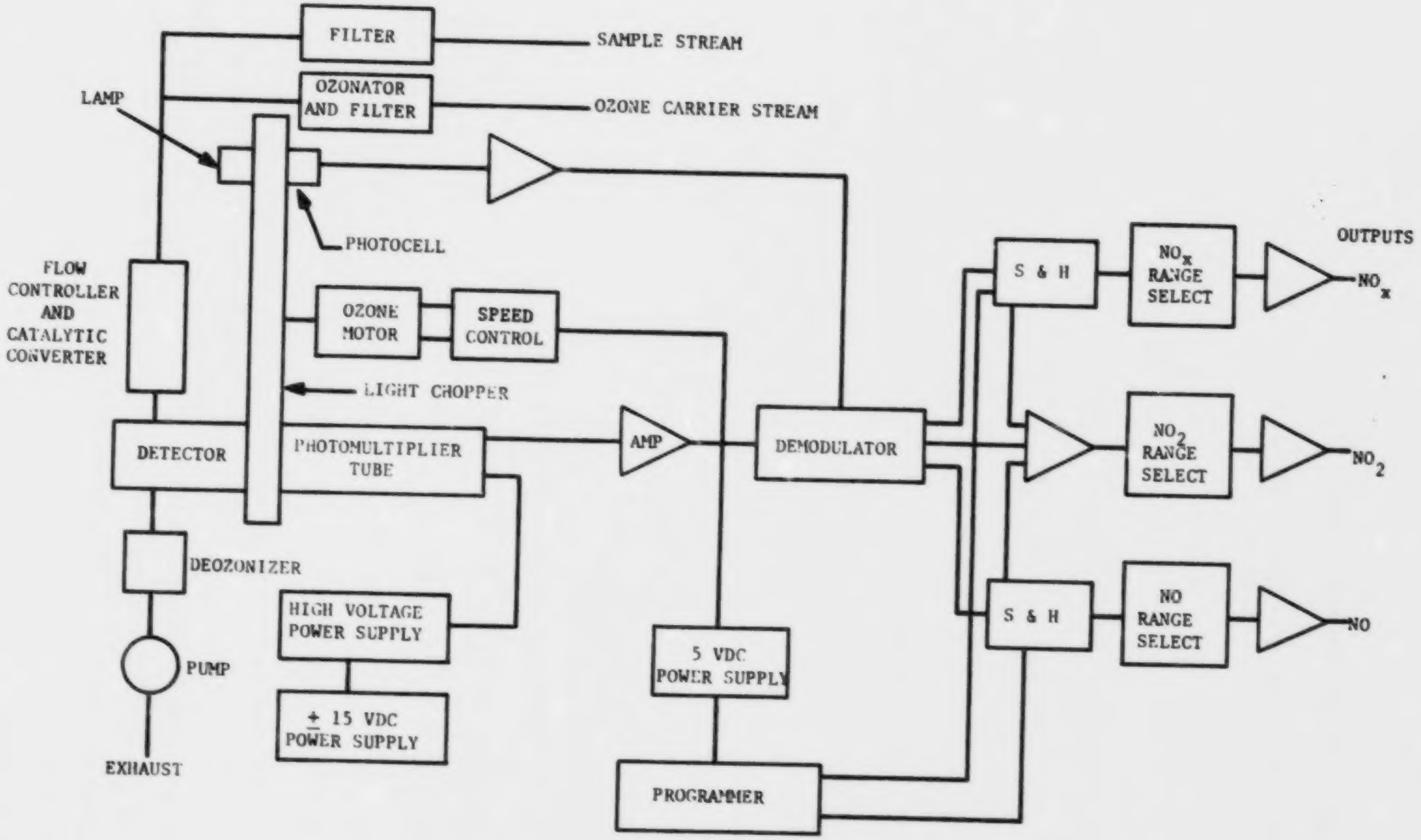

FILTER
SAMPLE STREAM
OZONATOR AND FILTER
OZONE CARRIER STREAM
LAMP
PHOTOCELL
FLOW CONTROLLER AND CATALYTIC CONVERTER
OZONE MOTOR
SPEED CONTROL
LIGHT CHOPPER
DETECTOR
PHOTOMULTIPLIER TUBE
AMP
DEMODULATOR
DEOZONIZER
HIGH VOLTAGE POWER SUPPLY
± 15 VDC POWER SUPPLY
PUMP
EXHAUST
5 VDC POWER SUPPLY
PROGRAMMER
S & H
S & H
NO_x RANGE SELECT
NO_2 RANGE SELECT
NO RANGE SELECT
OUTPUTS
NO_x
NO_2
NO

Figure 4.9: Block Diagram of Meloy Analyzer

(2) weight: 60 pounds (27.2 Kg);

(3) power requirements: 100 watts at 105 to 125 volts, 60 Hz;

(4) measurement ranges: 0.5, 1.0, 2.0, 5.0 ppm full scale (940 - 9400 μg/m^3);

(5) Mode selectors: ambient, zero, span;

(6) adjustments: zero and span potentiometers for NO, NO_x, and NO_2 outputs;

(7) outputs: 0-100 mV recorder; 0-1 VDC;

(8) stated performance specifications (manufacturer)

- (a) minimum detectable sensitivity: 0.015 ppm (28.2 μg/m^3);
- (b) linearity: ± 2%;
- (c) noise: 0.8% full scale of 0.5 ppm (940 μg/m^3) range;
- (d) precision: ± 2%;
- (e) accuracy: 0.01 ppm (18.8 μg/m^3);
- (f) zero drift: ± 3% per 7 days;
- (g) span drift: ± 2% per 7 days;
- (h) operational period: 7 or more days unattended;

(9) required accessories: stripchart recorder.

The gas flow system of the Meloy analyzer is composed of three parts: ambient air/ozone flow system and NO and NO_x sample air flow systems. A flow diagram is shown in Figure 4.10. Ozone concentrations (≈ 1000-3500 ppm) are generated via a high voltage ozone generator using ambient air scrubbed through a chemical filter. Separate NO and NO_x sample streams are provided through identical flow systems, except that in the case of NO_x the air stream passes through a catalytic converter. Constant flow rates are

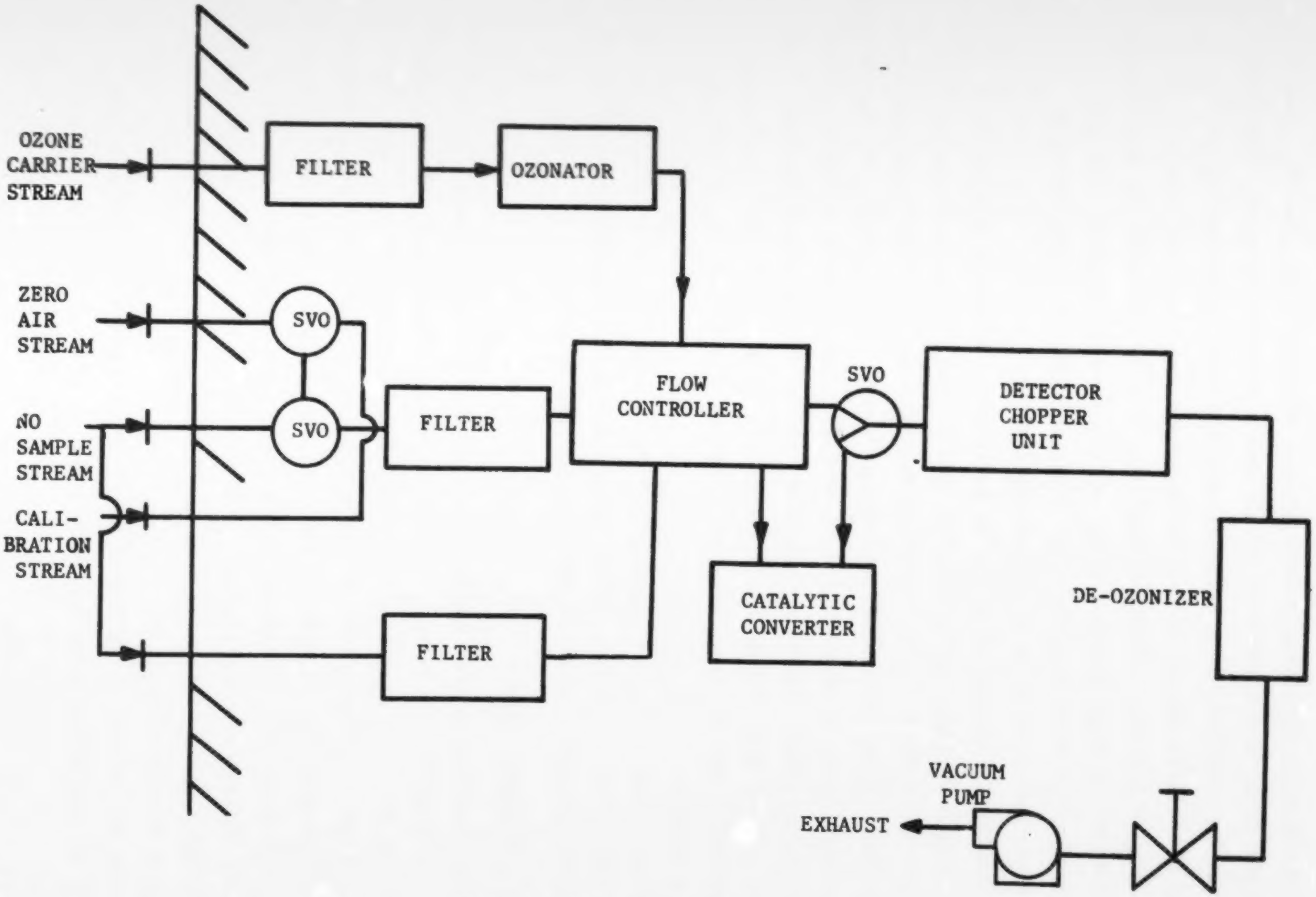

OZONE CARRIER STREAM
ZERO AIR STREAM
NO SAMPLE STREAM
CALI- BRATION STREAM
FILTER
OZONATOR
SVO
SVO
FILTER
FILTER
FLOW CONTROLLER
SVO
DETECTOR CHOPPER UNIT
CATALYTIC CONVERTER
DE-OZONIZER
VACUUM PUMP
EXHAUST

Figure 4.10: Meloy Flow Diagram

maintained through the three inlets (ozone, NO sample air, and NO_x sample air) by use of a flow controller module and a vacuum regulator. The flow controller is comprised of a temperature-controlled cartridge which presents a constant pneumatic impedance (stainless steel capillaries) to the NO, NO_x, and ozone carrier streams over a 5 to 40°C ambient temperature change. A vacuum regulator and pump are utilized to maintain the pneumatic system at a constant pressure. Particulates are prevented from entering the inlet lines by a 7μ particle filter.

The detector/chopper unit of the analyzer consists of a detector chamber, light chopper, and a photomultiplier tube. The functions of this unit are to provide a chamber in which the reaction can take place and to modulate and amplify the chemiluminescent signal. The detector arrangement has gas entry ports on one end and an optical window/filter arrangement and photomultiplier tube coupled to the other end of the detector chamber. The detector chamber and photomultiplier tube are separated by a light chopper, which modulates the dc chemiluminescent signal and transforms it into a pulsed dc signal.

The catalytic converter used in the Meloy analyzer to reduce NO_2 to NO contained copper sulfate and was maintained at a temperature of 300°C. Conversion efficiency of 95 to 98% was reported by Meloy.

4.4.2 Operational Summary

The chemiluminescent analyzer was installed in the mobile van on January 19, 1973 by the service representatives of Meloy and was operated continuously through July 16, 1973. During this period of time both short-term and long-term tests were performed on the analyzer in accordance with the test plan requirements. The frequency of performance monitoring during these tests was dependent on the particular requirements of the evaluation procedure being applied. Calibration frequency for short-term drift was on a daily basis, and that for longer term drift studies was on a weekly or biweekly basis.

During the six-month period in which the analyzer was operated and subjected to the performance evaluation tests, several failures occurred.

One failure involved conversion of NO_2 to NO by the heated stainless steel capillary used to regulate sample air flow rate and caused NO_2 interference with the NO measurement. This was considered a design deficiency and reported to Meloy. In addition, catalyst material was found deposited in the cell capillary and thereby reduced flow. The other failures, four in all, resulted from an underdesigned ozonator transformer. Insufficient insulation on the secondary winding resulted in a voltage breakdown and shorted out the transformer. The recommendation to upgrade the transformer was not heeded by Meloy and the defective part was simply replaced with the same model transformer. Routine maintenance involved replacement of the Teflon prefilter element on the sample inlet line, charcoal in the zero air scrubber, and silica gel and molecular sieve in the ozonator air cleanup scrubber on a monthly basis.

4.5 THERMO ELECTRON MODEL 14 CHEMILUMINESCENT NO-NO_x-NO_2 ANALYZER

4.5.1 Instrument Description

Operation of the Thermo Electron NO-NO_x-NO_2 analyzer is based on the flameless chemiluminescent reaction between NO and O_3:

$$NO + O_3 \rightarrow NO_2^* + O_2 \rightarrow NO_2 + h\nu \ .$$

Light emission resulting from the reversion of electronically excited NO_2 molecules to their ground state is directly proportional to the concentration of NO molecules involved in the reaction.

Basic components of the analyzer are a gas flow system, catalytic converter, reaction chamber, high-voltage ozone generator, thermoelectric-cooled photomultiplier tube, and associated electronic circuitry. To measure NO concentrations, the gas sample is mixed with ozone in the reaction chamber, and the resulting chemiluminescence is monitored through an optical filter by a high sensitivity photomultiplier tube. To measure NO concentrations (NO + NO_2 reduced to NO), the sample gas flow is diverted through a catalytic converter, with the resulting chemiluminescent response being linearly proportional to the NO_x concentration entering the converter. Nitric oxide and NO_x concentrations are alternately measured and stored in electronic circuits which automatically subtract the NO concentration from the NO_x concentration and display the NO_2 value continuously. Measurement of NO_2 via the reaction of NO with O_3 is not subject to interference from any of the common air pollutants found in ambient air, such as CO_2, CO, C_2H_4, NH_3, SO_2, and H_2O[9]; but recent evidence indicates a possible response to PAN (peroxy acetyl nitrate).

The physical characteristics and other descriptors of the Thermo Electron NO-NO_x-NO_2 analyzer are as follows:

(1) overall dimensions: 19 in (48.3 cm) width,
17 in (43.2 cm) height,
18 in (45.7 cm) depth;

(2) weight: 80 pounds (36.4 Kg);

(3) power requirements: 500 watts at 115 V, 60 Hz;

(4) measurement ranges: 0.05, 0.1, 0.25, 0.5, 1, 2.5. 5
and 10 ppm (94 to 18,800 $\mu g/m^3$);

(5) mode selectors: automatic mode (NO-NO_x-NO_2),
manual mode (NO or NO_x);

(6) adjustments: zero (background) and calibrate potentiometers;

(7) outputs: 0-10 V (NO, NO_x, NO_2 outputs);

(8) stated performance specifications (manufacturer);

    (a) minimum detectable sensitivity: not specified;

    (b) linearity: ± 1% full scale;

    (c) noise: not specified;

    (d) precision: precision of span setting better than 1%;

    (e) accuracy: not specified;

    (f) zero drift: < 1% in 24 hours;

(g) span stability: ± 1% in 24 hours,
± 3% in 7 days;

(h) operational period: not specified;

(9) required accessories: stripchart recorder.

The gas flow system of the Thermo Electron analyzer is composed of two separate systems, sample air and NO/NO_x flow systems. A flow diagram is shown in Figure 4.11. Ozone concentrations are generated by an electric discharge ozone generator using ambient air scrubbed through an air dryer. Sample air containing NO and NO_x enter the reaction chamber through either of two loops with the direction of flow controlled by a solenoid valve. In the NO_x mode of operation, sample air is diverted through the catalytic converter. Sample air and ozone flow rates are maintained constant by use of capillary restrictors, a bypass flow system, and two metal-bellows vacuum pumps. Constant flow to the reaction chamber is maintained by providing a differential pressure across a 20-mil capillary of approximately 22 in Hg (55.9 cm Hg). Stability of the instrument calibration is dependent on maintaining constant flow rates of sample and ozone and maintaining an absolute pressure of 8 in Hg (20.3 cm Hg) in the reaction chamber. Particulates are prevented from entering the instrument by a particulate filter.

The detector unit consists of a reaction chamber, optical filter, thermoelectric-cooled photomultiplier tube, electrometer, amplifier, memory, and comparator circuitry.

Three catalytic converters are available for use in the Thermo Electron analyzer. The recommended operating temperatures for the various converter options available are as follows:

Model 300 - Molybdenum Converter - 400°C
Model 325 - Carbon Converter - 300°C
Model 350 - Stainless Steel Converter - 400°C.

The standard converter supplied with the Model 14, unless otherwise specified, is the Model 350, Stainless Steel. Conversion efficiency of 98% has been reported.

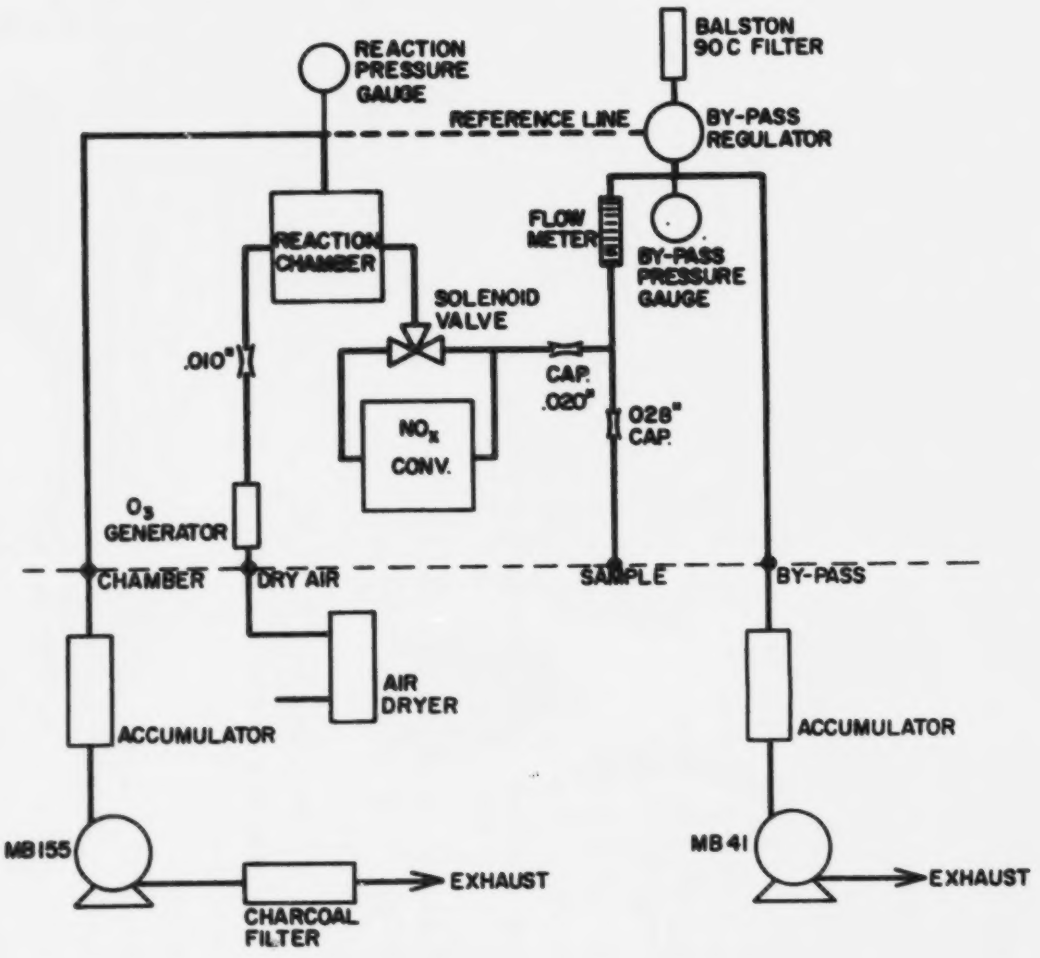

REACTION PRESSURE GAUGE
BALSTON 90C FILTER
REFERENCE LINE
BY-PASS REGULATOR
FLOW METER
REACTION CHAMBER
BY-PASS PRESSURE GAUGE
SOLENOID VALVE
.010"
CAP. .020"
NO_x CONV.
.028" CAP.
O_3 GENERATOR
CHAMBER
DRY AIR
SAMPLE
BY-PASS
AIR DRYER
ACCUMULATOR
ACCUMULATOR
MB155
MB41
CHARCOAL FILTER
EXHAUST
EXHAUST

Figure 4.11: Flow Schematic, Model 14 NO-NO_2-NO_x Analyzer

4.5.2 Operational Summary

The chemiluminescent analyzer was installed in the mobile van on May 8, 1973 and operated continuously through July 15, 1973. During this period of time both short-term and long-term tests were performed on the analyzer in accordance with the test plan requirements. The frequency of performance monitoring during these tests was dependent on the particular requirements of the evaluation procedure being applied. Calibration frequency for short-term drift was on a daily basis, and that for longer term drift studies was on a weekly or biweekly basis.

During the two-month period in which the analyzer was operated and subjected to the performance evaluation tests, one failure occurred which resulted from failure of the converter heater. The converter heater was promptly replaced and the evaluation continued. Routine maintenance consisted of replacement of the drierite in the air dryer for the ozone generator flow system.

4.6 REM MODEL 642 CHEMILUMINESCENT $NO-NO_x-NO_2$ ANALYZER

4.6.1 Instrument Description

Operation of the Rem $NO-NO_x-NO_2$ analyzer is based on the flameless chemiluminescent reaction between NO and O_3:

$$NO + O_3 \rightarrow NO_2^* + O_2 \rightarrow NO_2 + h\nu.$$

The intensity of the radiation of the electronically excited NO_2^* molecules as they revert to lower energy states is directly proportional to the concentration of NO molecules involved in the reaction.

Basic components of the analyzer are a reaction chamber, photomultiplier tube with thermoelectric cooler, filter, catalytic converter, gas flow system, electric discharge ozone generator, and electronic circuitry and amplifier systems as shown in Figure 4.12. Sample air and ozone are mixed and chemically react within the detector chamber, which is

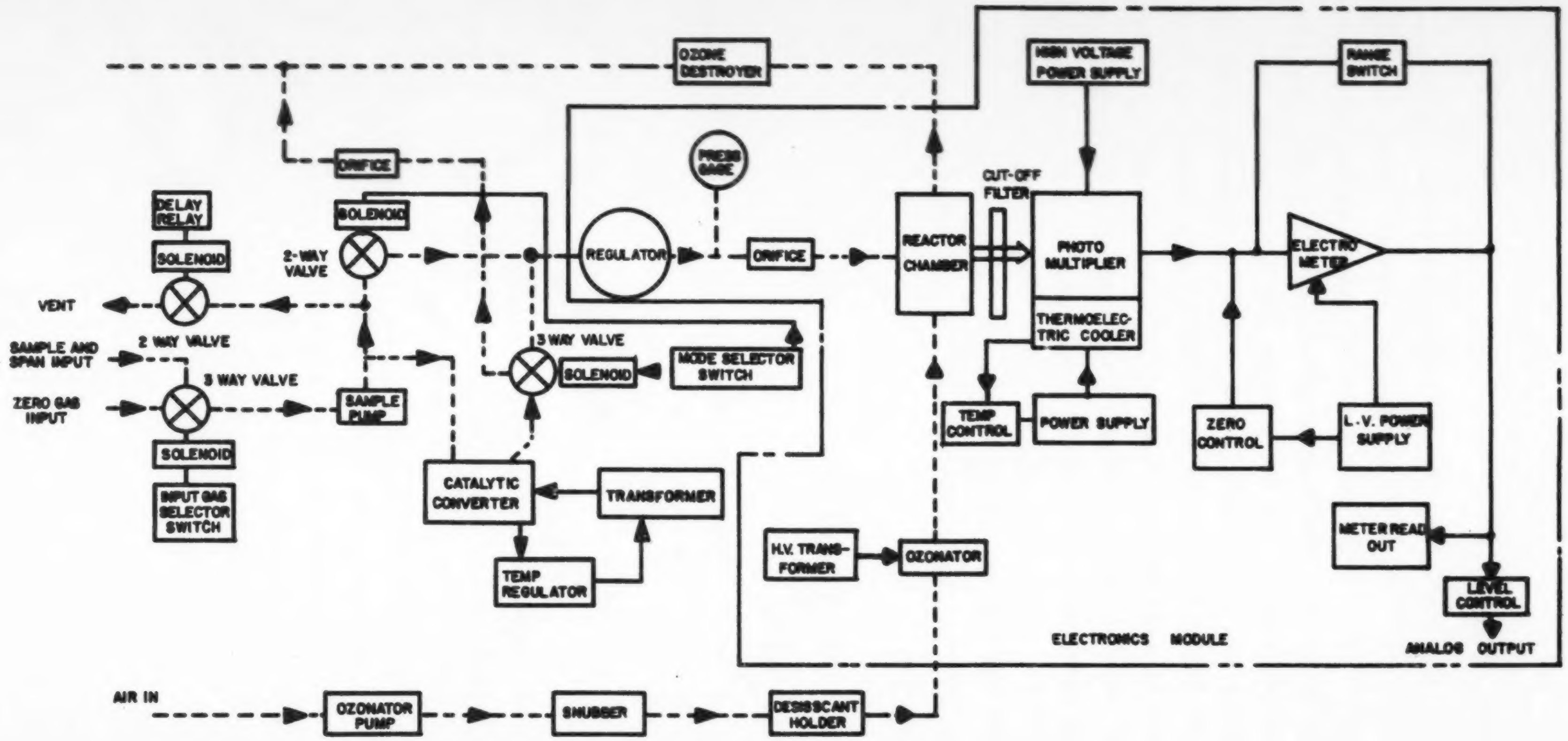

OZONE DESTROYER
HIGH VOLTAGE POWER SUPPLY
RANGE SWITCH
PRESS GAGE
ORIFICE
DELAY RELAY
SOLENOID
SOLENOID
2-WAY VALVE
REGULATOR
ORIFICE
REACTOR CHAMBER
CUT-OFF FILTER
PHOTO MULTIPLIER
ELECTRO METER
VENT
2 WAY VALVE
SAMPLE AND SPAN INPUT
3 WAY VALVE
ZERO GAS INPUT
3 WAY VALVE
SOLENOID
MODE SELECTOR SWITCH
THERMOELECTRIC COOLER
SAMPLE PUMP
TEMP CONTROL
POWER SUPPLY
ZERO CONTROL
L.V. POWER SUPPLY
SOLENOID
INPUT GAS SELECTOR SWITCH
CATALYTIC CONVERTER
TRANSFORMER
H.V. TRANSFORMER
OZONATOR
METER READ OUT
TEMP REGULATOR
LEVEL CONTROL
ELECTRONICS MODULE
ANALOG OUTPUT
AIR IN
OZONATOR PUMP
SNUBBER
DESISSCANT HOLDER

Figure 4.12: Rem System Flow Diagram

coupled to the cathode face of a photomultiplier tube. Detection of the light emission from the reaction yields a signal whose amplitude is proportional to the concentration of NO in the sample stream. The concentration of NO_2 in the ambient air sample is determined after quantitative conversion to NO, when the sample air stream is diverted through a catalytic converter. The detector alternately measures NO and total oxides of nitrogen (NO + NO_2 reduced to NO), 30 seconds in each mode. By electronic subtraction of the NO signal from the NO_x signal, the concentration of NO_2 in the air sample is determined. Total time for the measurement cycle is one minute. Measurement of NO_2 by the reaction of NO with O_3 is not subject to interference from any of the common air pollutants found in ambient air, such as CO_2, CO, C_2H_4, NH_3, SO_2, and H_2O[9]; but recent evidence indicates a possible response to PAN (peroxy acetyl nitrate).

The physical characteristics and other descriptors of the Rem NO-NO_x-NO_2 analyzer are as follows:

(1) overall dimensions: 19.6 in (49.8 cm) width,
16.5 in (41.9 cm) height,
18 in (46 cm) depth;

(2) weight: 125 pounds (56.8 Kg);

(3) power requirements: 350 watts at 115 ± 110 Volts, 60 Hz;

(5) mode selectors: ambient, zero, span;

(6) adjustments: separate zero and span adjustments for NO, NO_x, and NO channels not provided;

(7) outputs: adjustable from 10 MV to 5 Volts full scale;

(8) stated performance specifications (manufacturer)

(a) minimum detectable sensitivity: 0.005 ppm ($9.4\ \mu g/m^3$);

(b) linearity: 1% for given range;

(c) noise: not specified

(d) precision: ± 1% of full scale;

(e) accuracy: not specified;

(f) zero drift: ± 1% per day,
± 2% per 3 days,
± 3% per month;

(g) span drift: ± 1% per day,
± 2% per 3 days,
± 3% per month;

(h) operational period: not specified;

(9) required accessories: stripchart recorder.

The gas flow system of the Rem analyzer is composed of three separate systems: (1) sample-span-zero gas system, (2) air ozonator system, and (3) exhaust system. The Rem analyzer operates at atmospheric pressure, with sample air being provided via a metal-bellows pressure/vacuum pump. Components of the gas handling system are the sample pump, pressure regulator, and 600 cc/min orifice. Constant sample flow rate is achieved by a pressure drop across the 600 cc/min critical flow type orifice of at least 2 to 1. Constant pressure is maintained by the sample pump and pressure regulator which is set at 20 psig. Under these conditions the reaction chamber is essentially at atmospheric pressure. Ozonated air is provided through a separate system which consists of a pump, snubber, air dryer (drierite column), and an electric discharge ozonator. The exhaust gas system consists of a de-ozonizer and vent to the atmosphere. A gas flow diagram is shown in Figure 4.13. Particulates are prevented from entering the inlet lines by a 5μ Teflon particulate filter.

The detector cell of the analyzer consists of a reaction chamber, optical filter, thermoelectrically cooled photomultiplier tube (temperature controlled to 0°C), and detector cell housing. The optical filter prevents the photomultiplier tube from responding to light produced by interfering reactions, while the function of the photomultiplier tube is to convert the low-level photons resulting from the flameless reaction to electrical energy and to amplify the electrical signal for further processing the electrometer amplifier, memory and comparator circuitry.

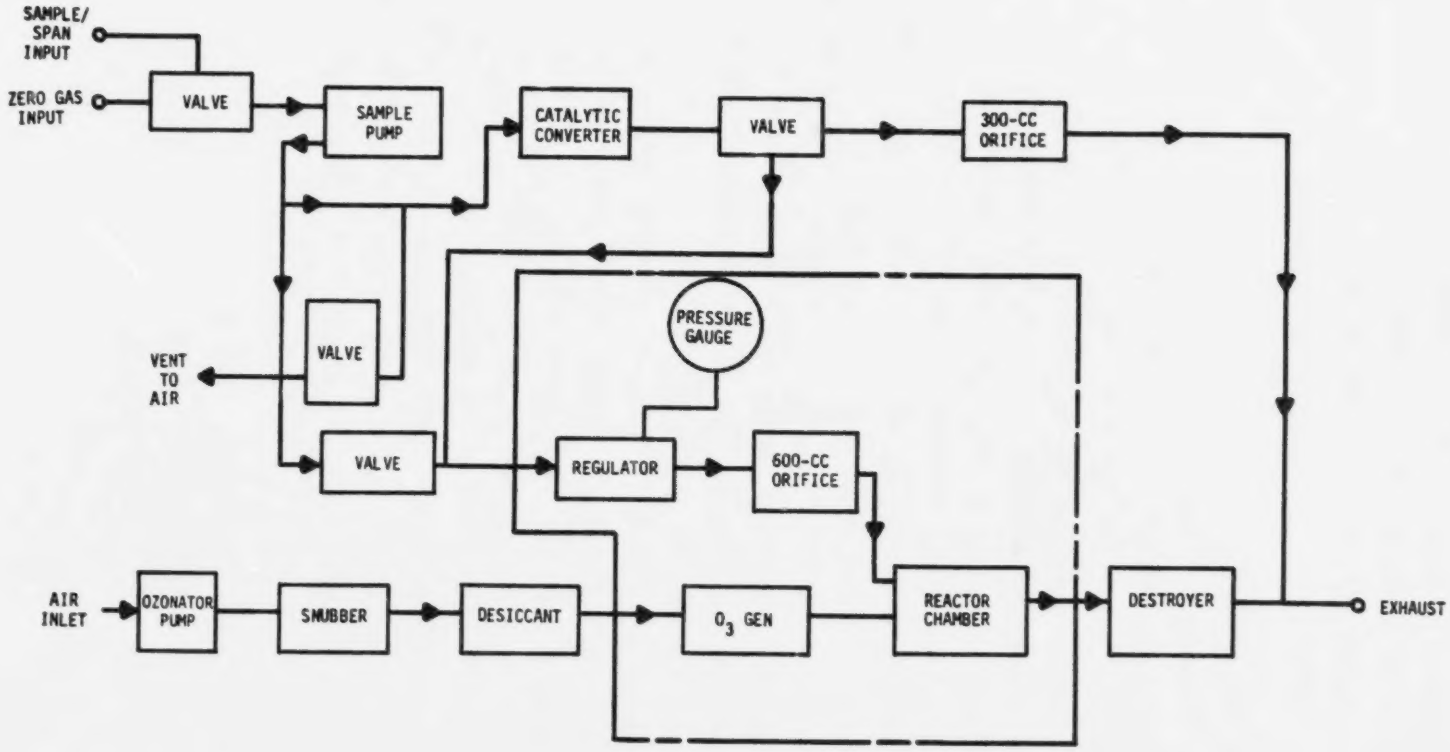

SAMPLE/ SPAN INPUT
ZERO GAS INPUT
VALVE
SAMPLE PUMP
CATALYTIC CONVERTER
VALVE
300-CC ORIFICE
VALVE
VENT TO AIR
PRESSURE GAUGE
VALVE
REGULATOR
600-CC ORIFICE
AIR INLET
OZONATOR PUMP
SNUBBER
DESICCANT
O_3 GEN
REACTOR CHAMBER
DESTROYER
EXHAUST

Figure 4.13: Rem Gas Flow Diagram

The Rem catalytic converter uses molybdenum to convert NO_2 to NO, and the temperature of the converter is maintained at 700°F. Rejuvenation of the catalytic converter with dry hydrogen is required when the converter efficiency drops below 95%.

4.6.2 Operational Summary

The chemiluminescent analyzer was installed in the mobile van on March 12, 1973 and operated continuously until May 7, 1973 at which time the analyzer was removed by Rem for modifications and replacement. During this period of time both short-term and long-term tests were performed on the analyzer in accordance with the test plan requirements. The frequency of performance monitoring during these tests was dependent on the particular requirements of the evaluation procedure being applied. Calibration frequency for short-term drift was on a daily basis, and that for longer term drift sudies was on a weekly or biweekly basis.

During the two-month period in which the analyzer was operated and subjected to the performance evaluation tests, two failures occurred. Both failures involved the electronic circuitry and amplifier systems and required service calls by Rem personnel. On May 7, 1973, after the second failure, Rem personnel removed the analyzer from the evaluation and were to replace it with an updated model within three days. The replacement analyzer was never submitted by Rem for reevaluation. As originally designed, the Rem analyzer required an excessive amount of maintenance. Routine maintenance involved replacing the drierite in the drying column for the ozonator air supply at two-day intervals and regenerating the catalytic converter with hydrogen at 30-day intervals. Replacement of the particulate filter element of the air sample filter was required at periodic intervals.

4.7 MELOY MODEL SA-185R FLAME PHOTOMETRIC TOTAL SULFUR ANALYZER

4.7.1 Instrument Description

Operation of the Meloy Model SA-185R analyzer is based on the flame photometric principle, previously described in the literature[10,11]. The flame photometric principle utilizes detection of the 394-nm centered band emitted by sulfur-containing compounds when burned in a hydrogen-rich flame, thus creating an excited state species of sulfur. The resultant release of light energy when the species returns to ground state sulfur is measured by a photomultiplier tube that is optically shielded from the flame by the geometric arrangement of the detector and a narrow band-pass interference filter. The response of the detector is directly related to the concentration of sulfur entering the detector per unit time.

Basic components of the analyzer are a gas flow system, burner chamber, photomultiplier tube and hydrogen restrictor line enclosed in a thermoelectric cooler oven (temperature maintained at 20°C), linearizer network (converts log output of sulfur concentration versus output voltage to linear output voltage), hydrogen shut-off valve, and additional electronic circuitry and amplifier systems. A block diagram of the flame photometric analyzer is shown in Figure 4.14.

The physical characteristics and other descriptors of the Meloy SA-185R analyzer are as follows:

(1) overall dimensions: 19.0 in (48.2 cm) width,
10.0 in (25.4 cm) height,
17.0 in (43.2 cm) depth;

(2) weight: 60 pounds (27.2 Kg);

(3) power requirements: 350 watts at 115 ± 10% Volts, 60 Hz;

(4) measurement ranges: 0.01 to 1.0 ppm (26.1 to 2612 $\mu g/m^3$);

(5) mode selectors: ambient, zero, calibrate;

(6) adjustments: zero and span potentiometers;

(7) outputs: 0-1 Volt;

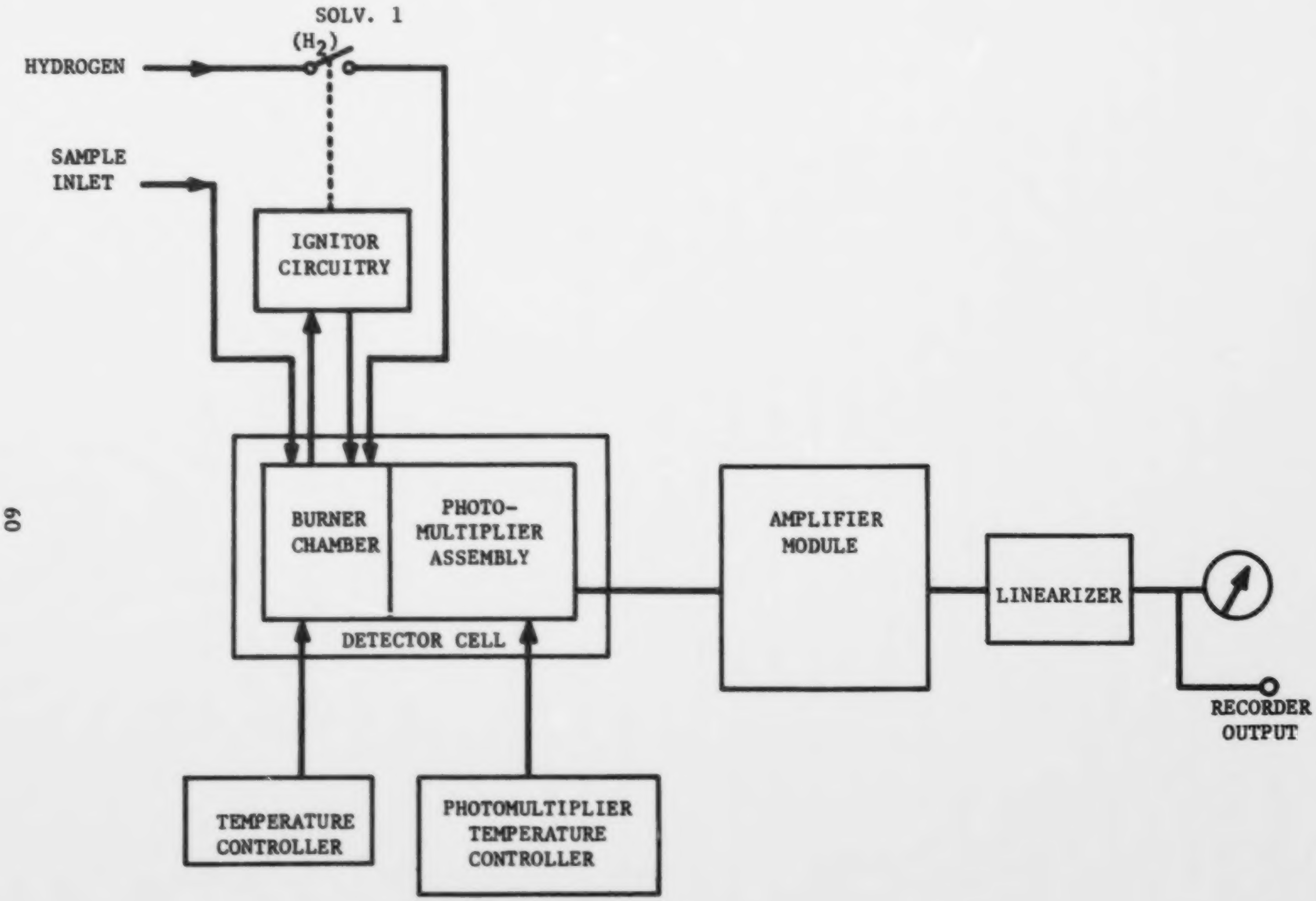

SOLV. 1
(H_2)
HYDROGEN
SAMPLE INLET
IGNITOR CIRCUITRY
BURNER CHAMBER
PHOTO-MULTIPLIER ASSEMBLY
DETECTOR CELL
AMPLIFIER MODULE
LINEARIZER
RECORDER OUTPUT
TEMPERATURE CONTROLLER
PHOTOMULTIPLIER TEMPERATURE CONTROLLER

Figure 4.14: Block Diagram of Meloy Flame Photometric Analyzer

(8) stated performance specifications (manufacturer)

   (a) minimum detectable sensitivity: < 0.01 ppm (26.1 $\mu g/m^3$);

   (b) linearity: not specified;

   (c) noise: not specified;

   (d) precision: ± 1% or better at full scale;

   (e) accuracy: not specified;

   (f) zero/span drift: not specified;

   (g) operational period: 14 days or more--limited by hydrogen supply;

(9) required accessories: supply of hydrogen gas; stripchart recorder.

The gas flow system of the Meloy analyzer is composed of two parts, hydrogen and sample air flow. Hydrogen passes from an external source (cylinder or H_2 generator) to the H_2 flow control valve or through the optional pressure regulator which maintains 125 cc/min H_2 flow. In either case, hydrogen flow is indicated on the rotameter. If the optional pressure regulator is used, a capillary restrictor is located in the thermoelectric cooler oven and maintained at 20°C. A schematic diagram of the gas flow system with and without options is shown in Figure 4.15 and Figure 4.16, respectively. The ambient air/calibration gas sample can be brought in through either the direct inlet line or the metered inlet line. During normal operation sample air is drawn into the burner chamber through the direct sample line. Exhaust gases from the burner chamber are diluted with ambient air, and the exhaust line is heated to prevent condensation of moisture in the pump. A hydrogen shut-off valve is available, which discontinues H_2 flow upon flame-out or power failure.

The detector cell of the analyzer consists of a burner chamber thermoelectrically-cooled photomultiplier tube optically shielded from the flame by a narrow band-pass interference filter, electrometer amplifier,

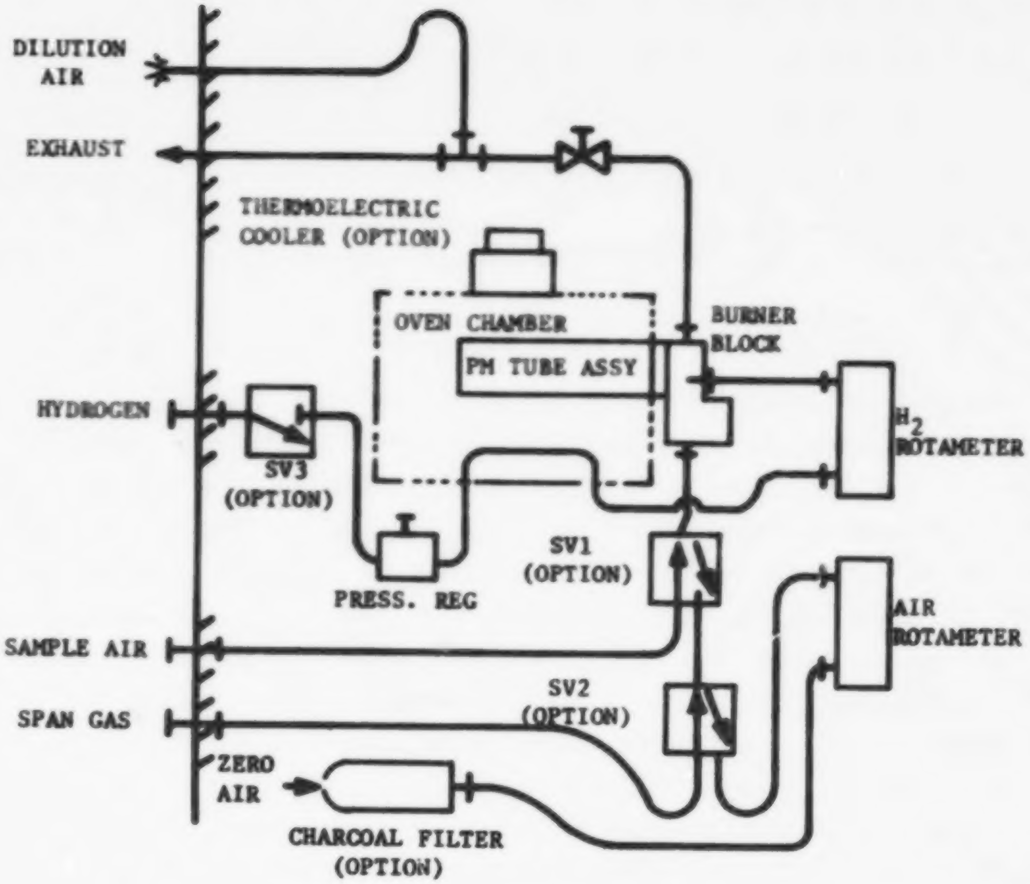

DILUTION AIR
EXHAUST
THERMOELECTRIC COOLER (OPTION)
OVEN CHAMBER
PM TUBE ASSY
BURNER BLOCK
H_2 ROTAMETER
HYDROGEN
SV3 (OPTION)
PRESS. REG
SV1 (OPTION)
AIR ROTAMETER
SAMPLE AIR
SV2 (OPTION)
SPAN GAS
ZERO AIR
CHARCOAL FILTER (OPTION)

Figure 4.15: Gas Flow Diagram (with options)

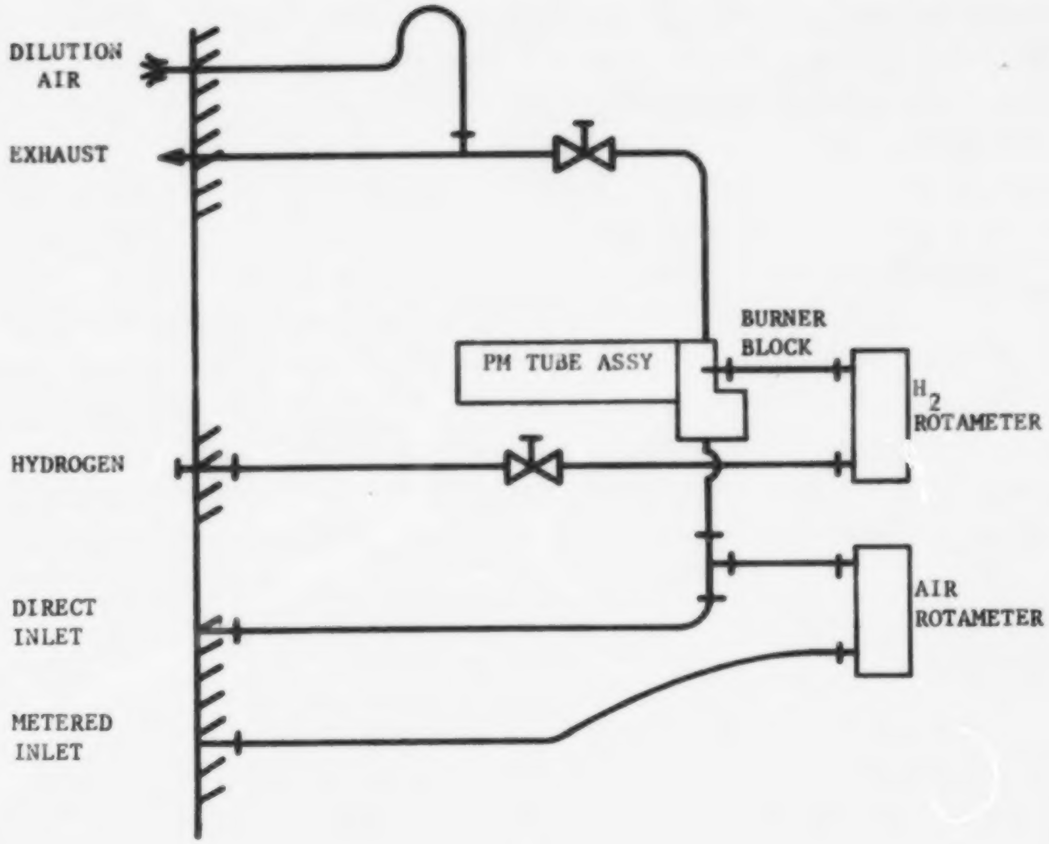

DILUTION AIR
EXHAUST
BURNER BLOCK
PM TUBE ASSY
H_2 ROTAMETER
HYDROGEN
AIR ROTAMETER
DIRECT INLET
METERED INLET

Figure 4.16: Gas Flow Diagram (without options)

and linearizer network. The purpose of the linearizer network is to convert the log output (sulfur concentration versus output voltage) to a linear output voltage in the range 0 to 1 V for sulfur concentrations of 0.01 to 1.0 ppm (28.1 to 2612 μg/m^3). The linearizer is used in conjunction with electrometer's log scale only and operates over the range 0 to 1 V.

4.7.2 Operational Summary

The flame photometric analyzer was installed in the mobile van on December 15, 1972 and operated continuously until May 14, 1973. During this period of time both short-term and long-term tests were performed on the analyzer in accordance with the test plan requirements. The frequency of performance monitoring during these tests was dependent on the particular requirements of the evaluation procedure being applied. Calibration frequency for short-term drift was on a daily basis, and that for longer term drift studies was on a weekly or biweekly basis.

During the five-month period in which the analyzer was operated and subjected to the performance evaluation tests, no failures occurred and a minimum amount of maintenance was required. Routine maintenance involved replacement of the Teflon prefilter element on the sample inlet line on a monthly basis and replacement of hydrogen cylinders (if used) when the pressure decreased to 100 psig.

4.8 BENDIX MODEL 8300 FLAME PHOTOMETRIC TOTAL SULFUR ANALYZER

4.8.1 Instrument Description

Operation of the Bendix Model 8300 analyzer is based on the flame photometric detection principle. The flame photometric principle utilizes detection of the 394-nm centered band emitted by sulfur-containing compounds when burned in a hydrogen rich flame, thus creating an excited state species of sulfur. The resultant release of light energy when the species returns to ground state sulfur is measured by a photomultiplier tube that is optically shielded from the flame by the geometric arrangement of the detector and a narrow band-pass interference filter. The response of the detector is directly related to the concentration of sulfur entering the detector per unit time.

Basic components of the analyzer are a gas flow system, burner chamber, photomultiplier tube with thermoelectric cooling (temperature maintained at 5°C), linearizer network (converts log output of sulfur concentration versus output voltage) to linear output voltage, hydrogen shut-off valve, and additional electronic circuitry and amplifier systems. A block diagram of the flame photometric analyzer is shown in Figure 4.17.

The physical characteristics and other descriptors of the Bendix total sulfur analyzer are as follows:

(1) overall dimensions: 17.6 in (44.8 cm) width,
8.5 in (21.5 cm) height,
17.0 in (43.0 cm) depth;

(2) weight: 60 pounds (27.2 Kg);

(3) power requirements: 300 watts at 115 ± 10% Volts, 60 Hz;

(4) measurement ranges: 0.01 to 1.0 ppm (26.1 to 2612 $\mu g/m^3$);

(5) mode selectors: ambient;

(6) adjustments: zero and span adjustment potentiometers;

(7) outputs: 0-10 MV (front panel); 0-1 V (rear panel);

(8) stated performance specifications (manufacturer)

  (a) minimum detectable sensitivity: 0.005 ppm (13.1 $\mu g/m^3$);

  (b) linearity: ± 1%;

  (c) noise: 0.5% of full scale;

  (d) precision: ± 1% of full scale;

  (e) accuracy: ± 2% of full scale;

  (f) zero/span drift: less than ± 1% per 24 hours,
  less than ± 2% per 3 days;

  (g) operational period: 7 or more days unattended;

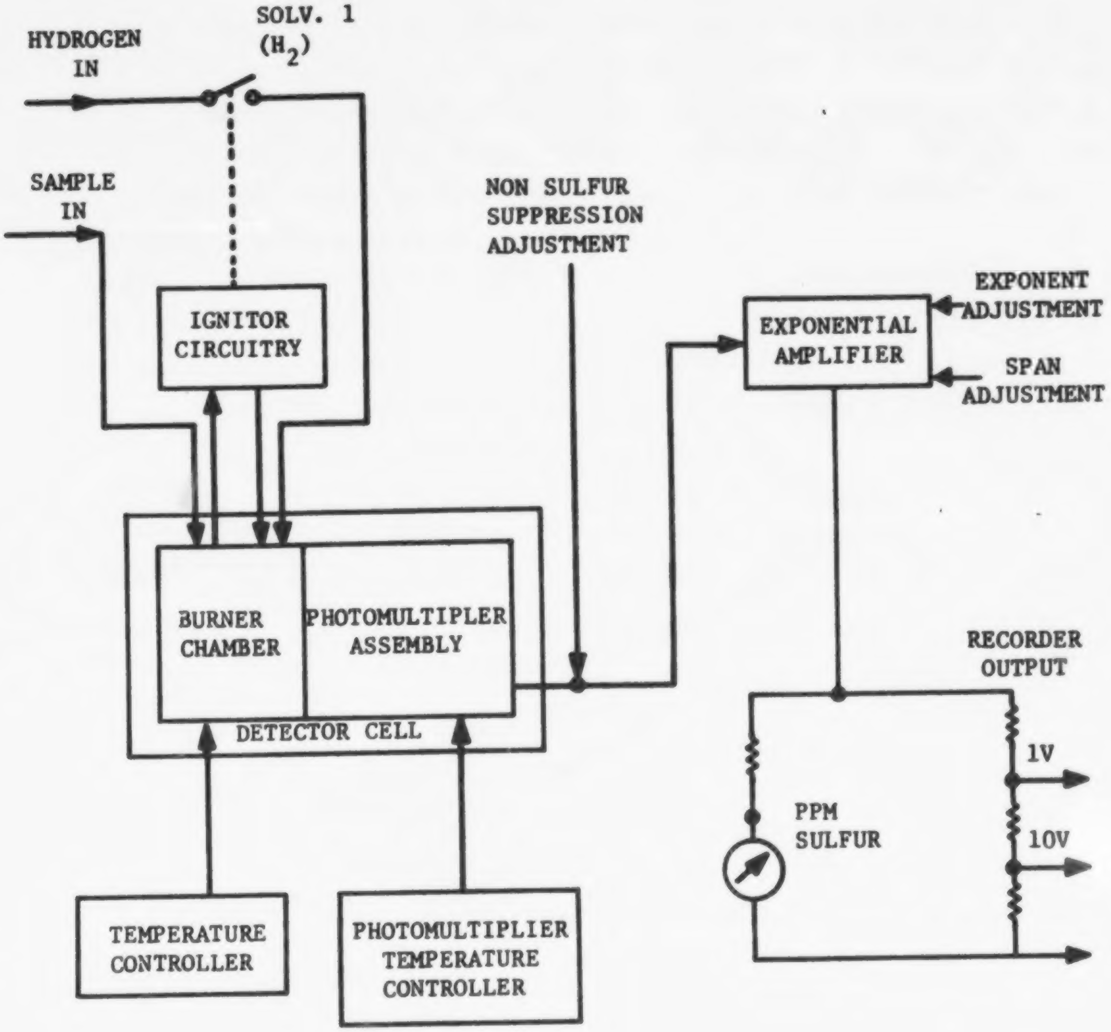

HYDROGEN IN
SOLV. 1
(H_2)
SAMPLE IN
IGNITOR CIRCUITRY
NON SULFUR SUPPRESSION ADJUSTMENT
EXPONENTIAL AMPLIFIER
EXPONENT ADJUSTMENT
SPAN ADJUSTMENT
BURNER CHAMBER
PHOTOMULTIPLER ASSEMBLY
DETECTOR CELL
RECORDER OUTPUT
1V
PPM SULFUR
10V
TEMPERATURE CONTROLLER
PHOTOMULTIPLIER TEMPERATURE CONTROLLER

Figure 4.17: Total Sulfur Analyzer Functional Block Diagram

(9) required accessories: supply of hydrogen gas; dryer and pressure regulator for hydrogen supply; stripchart recorder.

The gas flow system of the Bendix analyzer is composed of two parts, hydrogen and sample air flow. Hydrogen passes from an external source (cylinder or H_2 generator) to the H_2 flow control valve, through a capillary restrictor and rotameter, and into the burner chamber. The ambient air and/or calibration gas sample can be brought in through either the direct inlet line or the metered inlet line. During normal operation sample air is drawn into the burner chamber through the direct sample line. A schematic diagram of the gas flow system is shown in Figure 4.18. Exhaust gases from the burner chamber are diluted with ambient air, and the exhaust line is heated to prevent condensation of moisture in the pump. A hydrogen shut-off valve is available, which discontinues H_2 flow upon flame-out or power failure. Particulates are prevented from entering the inlet line by a 5μ particulate filter (Teflon).

The detector cell of the analyzer consists of a burner chamber, thermoelectrically cooled photomultiplier tube optically shielded from the flame by a narrow band-pass interference filter, electrometer amplifier and linearizer network. The purpose of the linearizer network is to convert the log output (sulfur concentration versus output voltage) to a linear output voltage in the range 0 to 1 V for sulfur concentrations of 0.01 to 1.0 ppm (28.1 to 2612 $\mu g/m^3$). The linearizer is used in conjunction with electrometer's log scale only and operates over the range 0 to 1 V.

4.8.2 Operational Summary

The flame photometric analyzer was installed in the mobile van on December 27, 1972 and operated continuously until May 14, 1973. During this period of time both short-term and long-term tests were performed on the analyzer in accordance with the test plan requirements. The frequency of performance monitoring during these tests was dependent on the particular requirements of the evaluation procedure being applied. Calibration frequency for short-term drift was on a daily basis, and that for longer term drift studies was on a weekly or biweekly basis.

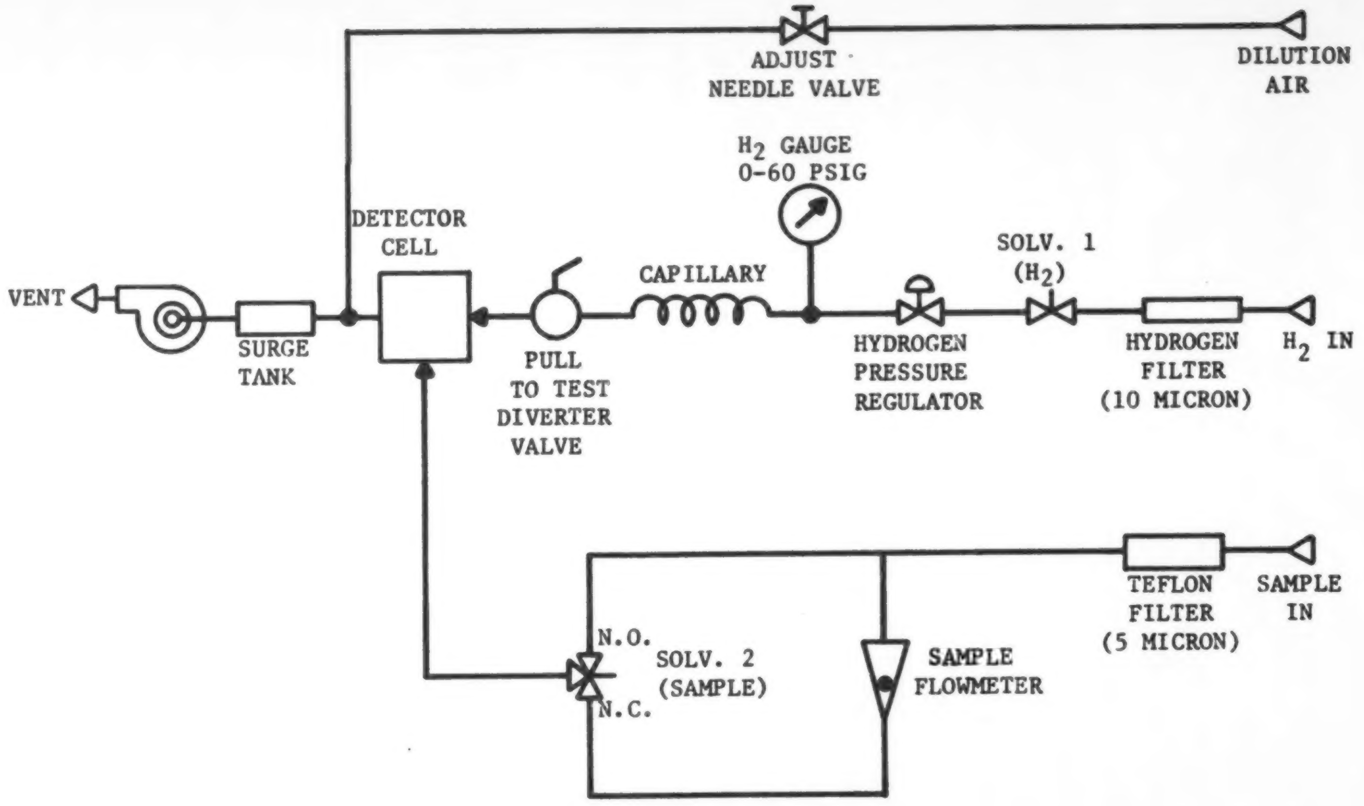

ADJUST
NEEDLE VALVE
DILUTION
AIR
H_2 GAUGE
0-60 PSIG
DETECTOR
CELL
SOLV. 1
(H_2)
CAPILLARY
VENT
SURGE
TANK
PULL
TO TEST
DIVERTER
VALVE
HYDROGEN
PRESSURE
REGULATOR
HYDROGEN
FILTER
(10 MICRON)
H_2 IN
TEFLON
FILTER
(5 MICRON)
SAMPLE
IN
N.O.
N.C.
SOLV. 2
(SAMPLE)
SAMPLE
FLOWMETER

Figure 4.18: Total Sulfur Analyzer Flow Diagram

During the five-month period in which the analyzer was operated and subjected to the performance evaluation tests, one failure occurred and required readjustment of the linearizing network. Routine maintenance involved replacement of the Teflon prefilter element on the sample inlet line on a monthly basis, replacement of hydrogen cylinders (if used) when the pressure decreased to 100 psig, and replacement of the molecular sieve drying column on the hydrogen supply line at periodic intervals.

4.9 BECKMAN MODEL 6800 AIR QUALITY CHROMATOGRAPH THC, CH_4, CO ANALYZER

4.9.1 Instrument Description

The Beckman Model 6800 Air Quality Chromatograph utilizes an automatic gas chromatographic flame ionization detector (GC-FID) to measure total hydrocarbons, methane, and carbon monoxide in ambient air. The analyzer is comprised of a gas sampling valve, a back flush valve, a pre-column, a molecular sieve column, a catalytic reactor, and a flame ionization detector (FID). Measured volumes of air are delivered at five-minute intervals to the FID to determine its total hydrocarbon content. An aliquot of the same air sample is introduced into the pre-column (stripper column) which removes carbon dioxide, water, and heavy hydrocarbons other than methane and prevents them from reaching the molecular sieve column. Methane and carbon monoxide are passed to a gas chromatographic column where they are separated. Methane is eluted first and passes unchanged through the catalytic reduction tube. Carbon monoxide is eluted into the catalytic reduction tube where it is reduced to methane prior to passing through the FID. Between analyses, the stripper column is backflushed to prepare it for subsequent analysis. A nickel catalyst is used in the reduction tube with hydrogen as the carrier gas to satisfy the requirements for the converter and also as a fuel for the FID.

The measuring electronics is comprised of all solid state devices which control all the timing functions such as valve switching, gating the amplifiers, and automatic attenuation for each pollutant. The analyzer is designed for semicontinuous operation and is capable of performing one analysis every five minutes. An instrument diagram is shown in Figure 4.19.

High specificity for the pollutants of interest is inherent in the hydrocarbon analyzer design. It is important that the hydrogen carrier gas be relatively free from CH_4, CO, C_2H_4, and C_2H_2 or exist in concentrations much less than the ambient levels to be measured.

The physical characteristics and other descriptors of the Beckman chromatograph are as follows:

(1) overall dimensions: 17 in (43.2 cm) width,
40 in (102 cm) height,
20 in (50.8 cm) depth;

(2) weight: ~175 lbs (79.4 Kg)

(3) power requirements: 500 watts, 107 to 127 Volts A.C. 50/60 Hz;

(4) measurement ranges: individually selectable, automatically actuated, ranges for each component; maximum sensitivity 1.0 ppm full scale;

(5) mode switch: sample or calibrate

operation: automatic repetitive analysis at selectable rate of 4, 6, or 12 analyses per hour for three component system;

(6) adjustment: independent span potentiometers for chromatograph and memory for each component;

(7) output: 0-10 MV recorder, 0-5 Vdc output from memory for trend record;

(8) stated performance specifications (manufacturer)

(a) minimum detectable sensitivity: not specified;

(b) linearity: 1% full scale;

(c) noise: not specified;

(d) precision: ± 0.5% of full scale or 0.05 ppm, whichever is greater

(e) accuracy: not specified;

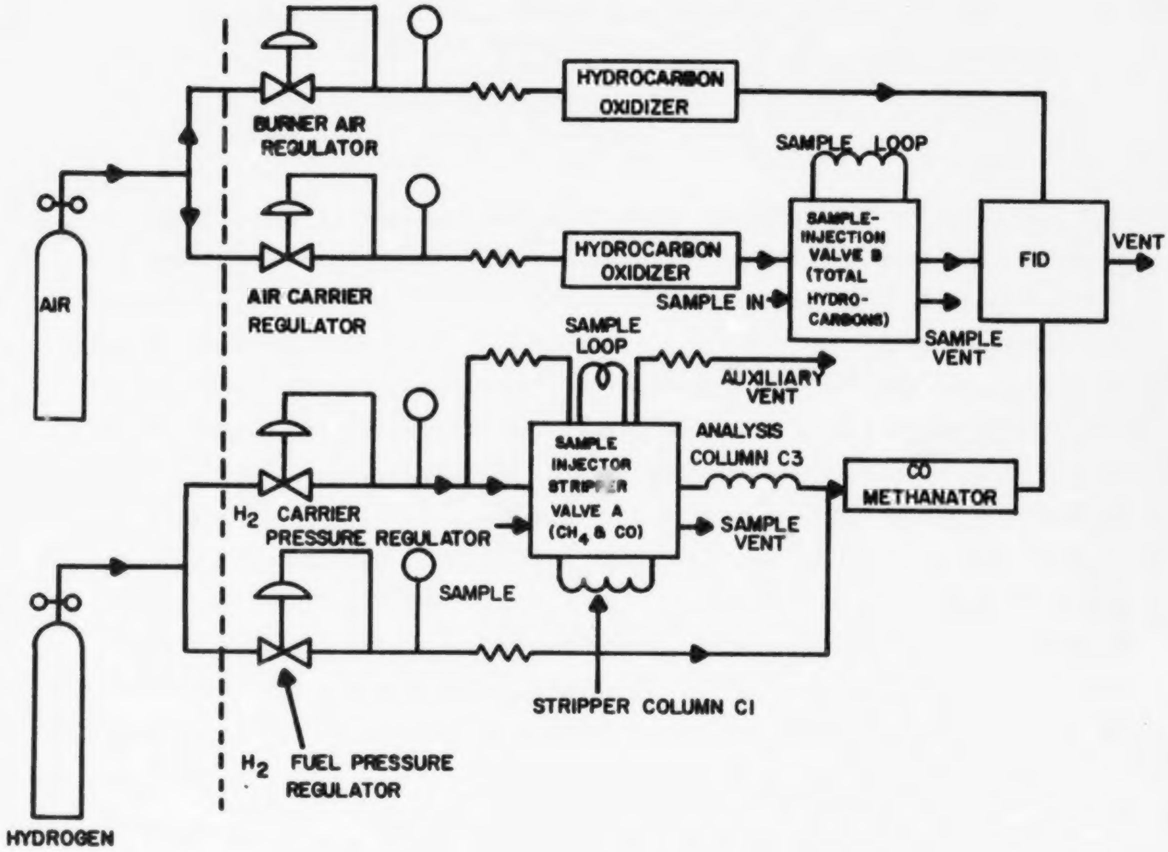

HYDROCARBON OXIDIZER
BURNER AIR REGULATOR
SAMPLE LOOP
SAMPLE-INJECTION VALVE B (TOTAL HYDRO-CARBONS)
HYDROCARBON OXIDIZER
FID
VENT
AIR
AIR CARRIER REGULATOR
SAMPLE IN
SAMPLE VENT
SAMPLE LOOP
AUXILIARY VENT
ANALYSIS COLUMN C3
SAMPLE INJECTOR STRIPPER VALVE A (CH_4 & CO)
CO METHANATOR
H_2 CARRIER PRESSURE REGULATOR
SAMPLE VENT
SAMPLE
STRIPPER COLUMN C1
H_2 FUEL PRESSURE REGULATOR
HYDROGEN

Figure 4.19: Schematic Diagram of Beckman 6800 Hydrocarbon Analyzer

(f) zero drift: automatic zero adjustment during each analysis cycle compensates for zero drift;

(g) span drift: not specified;

(h) operational period: not specified;

(i) operating temperature: 35°F to 120°F, 95% relative humidity;

(9) required accessories: hydrogen cylinder or generator, two-stage regulator, air supply or cylinder of compressed air.

The atmospheric sample is drawn into the analyzer by an internal metal-bellows pump. The pump provides a sample flow rate of 5 liters per minute; however, most of the ambient sample is released to the atmosphere to prevent pressurizing the sample loops. The Model 6800 consists of three sections: (1) gas control section, (2) chromatographic oven, and (3) electronic control section. Pressure regulators and associated gauges for air and hydrogen carrier gases, hydrogen fuel, air support gases for the FID, and service air to operate the slider valves are located on the front panel of the gas control section. The oven section contains the columns, slider valves, fan to equalize the temperature, and the flame ionization detector. The electronic control section includes circuitry for flame ignition, amplifiers for FID output signal, automatic control of all time-related functions, memory and analog presentation of data and power supplies.

4.9.2 Operational Summary

The Beckman chromatograph was installed in the mobile van on December 14, 1972 and operated continuously until June 29, 1973. During this period of time both short-term and long-term tests were performed on the analyzer in accordance with the test plan requirements. The frequency of performance monitoring during these tests was dependent on the particular requirements of the evaluation procedure being applied. Calibration frequency for short-term drift was on a daily basis, and that for long-term drift studies was on a weekly or biweekly basis.

During the six-month period in which the analyzer was operated and subjected to the performance evaluation tests, two failures occurred. The first failure involved a sticking valve slider, and the second involved the temperature controller for the oven. A minimum amount of maintenance was required during this period of time. Routine maintenance involved replacing the sample inlet filter element, maintaining the hydrogen generator, and replacing compressed air cylinders periodically.

4.10 BENDIX MODEL 8201 AMBIENT HYDROCARBON ANALYZER

4.10.1 Instrument Description

The Bendix ambient hydrocarbon analyzer utilizes a hydrogen flame ionization detector (FID) for the measurement of reactive hydrocarbons. The analyzer is capable of measuring total hydrocarbons, methane, and non-methane hydrocarbons by difference method (i.e., THC minus CH_4).

During the operation, a metered quantity of ambient air is routed from the sample inlet through the sample valves and a GC-column where methane is separated from the THC. Methane is then routed from the column into the FID to yield a measurement. A second quantity of ambient air is then routed from the sample inlet through the sampling valve directly to the FID, bypassing the analytical column. The value of the methane analysis is then electronically subtracted from the total hydrocarbon value, providing a measurement of non-methane hydrocarbons. Analytical functions and signal processing are programmed by a solid state electronic timer. The output is updated after each cycle which is approximately three minutes. The signals are stored in permanent memories that are updated after each cycle.

The physical characteristics and other descriptors of the Bendix hydrocarbon analyzer are as follows:

(1) overall dimensions: 17.6 in (44.8 cm) width,
9.2 in (23.4 cm) height,
17.2 in (43.8 cm) depth;

(2) weight: 50 lbs (22.7 Kg)

(3) power requirements: 700 watts maximum,
500 watts normal at
105-125 volts,
50 or 60 Hz;

(4) measurement ranges: 1, 2, 5, 10 ppm

(5) Mode switch: Sample or calibrate

(6) adjustment: zero and span adjustment potentiometers for THC, CH_4, THC-CH_4;

(7) outputs: 0-10 MV recorder, 0-1 Vdc;

(8) stated performance specifications (manufacturer)

- (a) minimum detectable sensitivity: 0.005 ppm;
- (b) linearity: ± 0.5%;
- (c) noise: ± 1%;
- (d) precision: ± 1% of full scale;
- (e) accuracy: ± 1% of full scale;
- (f) zero drift: ± 1% per 24 hours (automatically zeroed each cycle);
- (g) span drift: ± 1% per 24 hours or ± 2% per 3 days;
- (h) operational period: 7 or more days unattended
- (i) operating temperature fluctuations: ± 5°C
- (j) operating temperature extremes: 5°C to 40°C

(9) required accessories: cylinder of hydrogen or hydrogen generator, two-stage regulator, air supply unit with hydrocarbon oxidizer.

The instrument requires a source of clean air and a source of pure hydrogen. The hydrogen consumption is approximately 50 cc per minute.

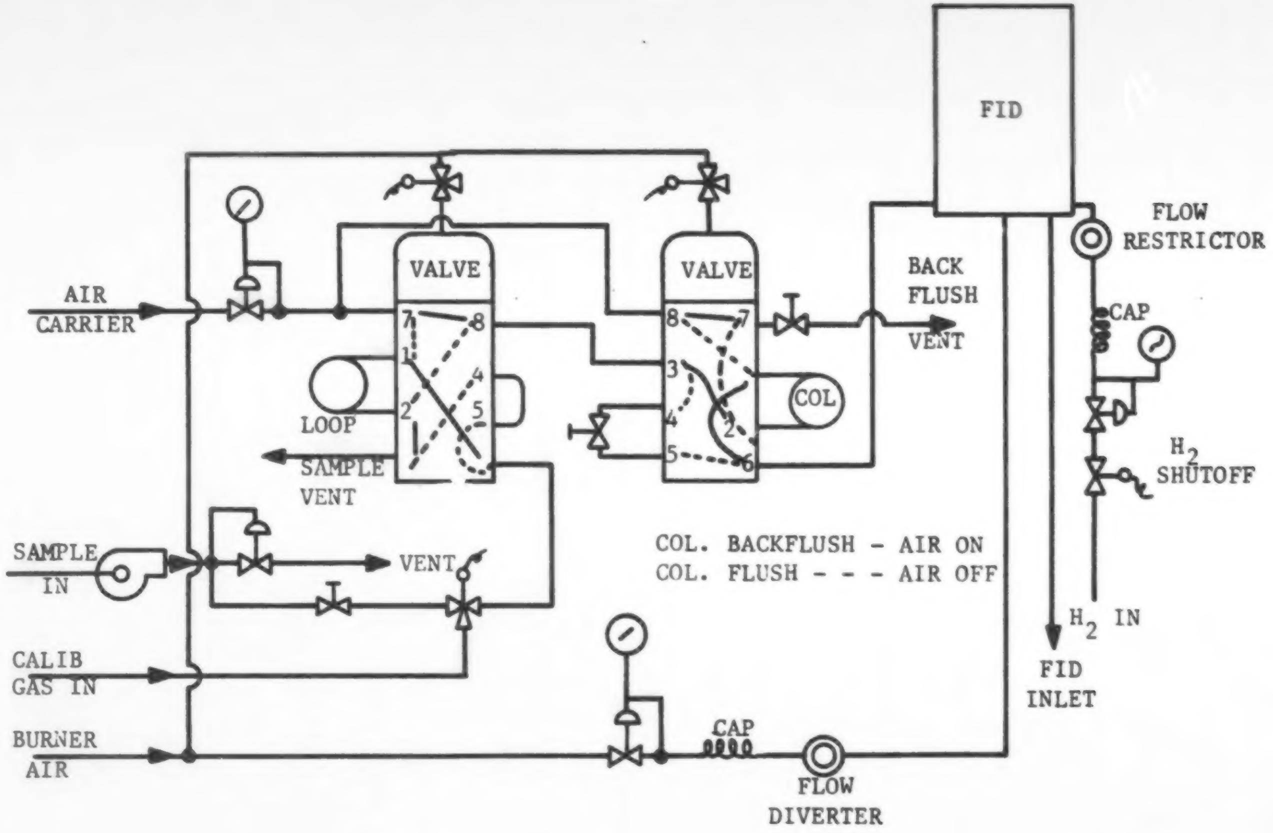

FID
VALVE
VALVE
AIR CARRIER
SAMPLE IN
CALIB GAS IN
BURNER AIR
LOOP
SAMPLE VENT
VENT
COL
BACK FLUSH VENT
FLOW RESTRICTOR
CAP
H_2 SHUTOFF
H_2 IN
FID INLET
CAP
FLOW DIVERTER
COL. BACKFLUSH - AIR ON
COL. FLUSH - - - AIR OFF
1
2
4
5
7
8
2
3
4
5
6
7
8

Figure 4.20: Analytical Flow Diagram

Sample flow rate is approximately 200 cc per minute. The analyzer flow diagram is shown in Figure 4.20.

Automatic zeroing of the detector output is accomplished during each cycle to ensure a stable baseline for long-term, unattended operation.

4.10.2 Operational Summary

The hydrocarbon analyzer was installed in the mobile van on February 16, 1973 and operated continuously until July 19, 1973. During this period of time both short-term and long-term tests were performed on the analyzer in accordance with the test plan requirements. The frequency of performance monitoring during these tests was dependent on the particular requirements of the evaluation procedure being applied. Calibration frequency for short-term drift was on a daily basis, and that for long-term drift studies was on a weekly or biweekly basis.

During the five-month period in which the analyzer was operated and subjected to the performance evaluation tests, two failures occurred. One failure involved valve actuation, and the other failure resulted in loss of output signal. A minimum amount of maintenance was required during this period of time. Routine maintenance involved replacement of the Teflon filter on the sample inlet and maintaining hydrogen generator and/or cylinder replacement. The air supply unit operated for the five-month period with no failures.

4.11 BENDIX MODEL 8501-5FA CARBON MONOXIDE ANALYZER

4.11.1 Instrument Description

The Bendix carbon monoxide analyzer operates on the principle that CO has a sufficiently characteristic infrared absorption spectrum so that the absorption of infrared radiation by the CO molecule can be used to measure the CO concentration in the presence of other gases. A schematic diagram is shown in Figure 4.21. Optical beams from the infrared source travel through adjacent parallel cells, one beam for the sample cell and one for the reference cell. The infrared radiation from the radiation lamp

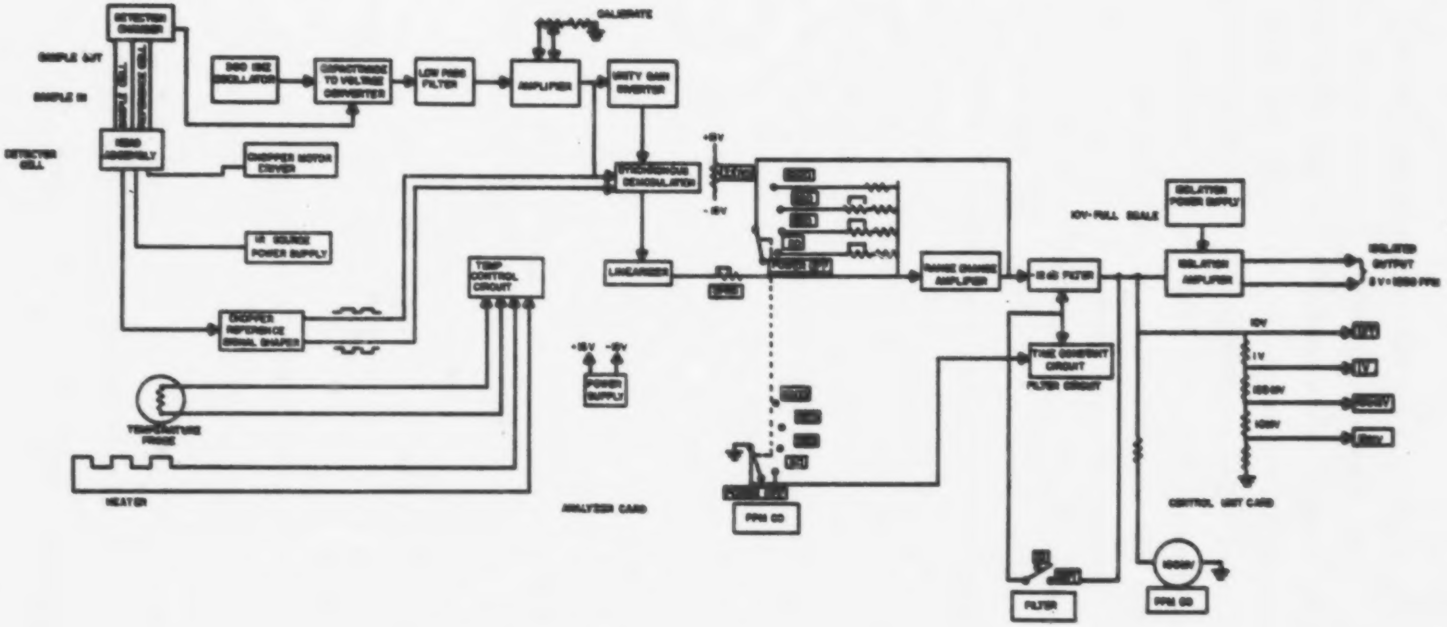

DETECTOR CHAMBER
SAMPLE OUT
SAMPLE IN
DETECTOR CELL
SOURCE ASSEMBLY
OSCILLATOR
CAPACITANCE TO VOLTAGE CONVERTER
LOW PASS FILTER
AMPLIFIER
CALIBRATE
UNITY GAIN INVERTER
CHOPPER MOTOR DRIVER
IR SOURCE POWER SUPPLY
SYNCHRONOUS DEMODULATOR
CHOPPER REFERENCE SIGNAL SHAPER
TEMP CONTROL CIRCUIT
TEMPERATURE PROBE
HEATER
+15V
-15V
POWER SUPPLY
ANALYZER CARD
LINEARIZER
PPM CO
RANGE CHANGE AMPLIFIER
10V-FULL SCALE
FILTER
TIME CONSTANT CIRCUIT
FILTER CIRCUIT
ISOLATION POWER SUPPLY
ISOLATION AMPLIFIER
ISOLATED OUTPUT
10V
1V
CONTROL UNIT CARD
FILTER
PPM CO

Figure 4.21: Infrared Gas Analyzer Block Diagram

is modulated in phase reversal by the rotating chopper into two equally intense portions. After passing through a diffuser, both radiation portions enter the detection chamber which contains the gas constituent to be measured. The reference cell is filled with nitrogen which does not absorb the infrared radiation. The gas mixture to be analyzed flows through the sample cell. The absorbed energies heat the gas in these chambers, causing the pressure of the gas to rise. The gas concentration in the two measuring chambers and the geometry of these chambers are such that the pressures are equal on both sides of the diaphragm capacitor when none of the constituent to be measured is in the analysis chamber. If, however, the radiation in the analysis chamber passes through a gas mixture containing CO, some of the specific radiation energy is absorbed, and the resulting reduction of radiation intensity takes place primarily in the center of the infrared absorption band. The condition disturbs the pressure equilibrium existing between the two chambers, and the pressure differential is proportional to the deflection of the diaphragm. This results in a change of measuring capacitor which is excited to vibration at a frequency corresponding to the radiation modulating chopper. The amplitude of this vibration is a measure of the gas concentration to be determined. The signal is further amplified, filtered, and demodulated to provide stable output. A diagram of the gas flow system is shown in Figure 4.22.

The physical characteristics and other descriptors of the Bendix CO analyzer are as follows:

(1) overall dimensions: 30 in (76 cm) height,
19 in (48 cm) width,
11 in (27 cm) depth;

(2) weight: 60 pounds (27.22 Kg);

(3) power requirements: 300 watts at 105-125 volts, 60 Hz;

(4) measurement ranges: 0-20, 50, 250, 500, 1000 ppm;

(5) mode switch: zero, ambient, calibrate;

(6) adjustments: zero and span potentiometers;

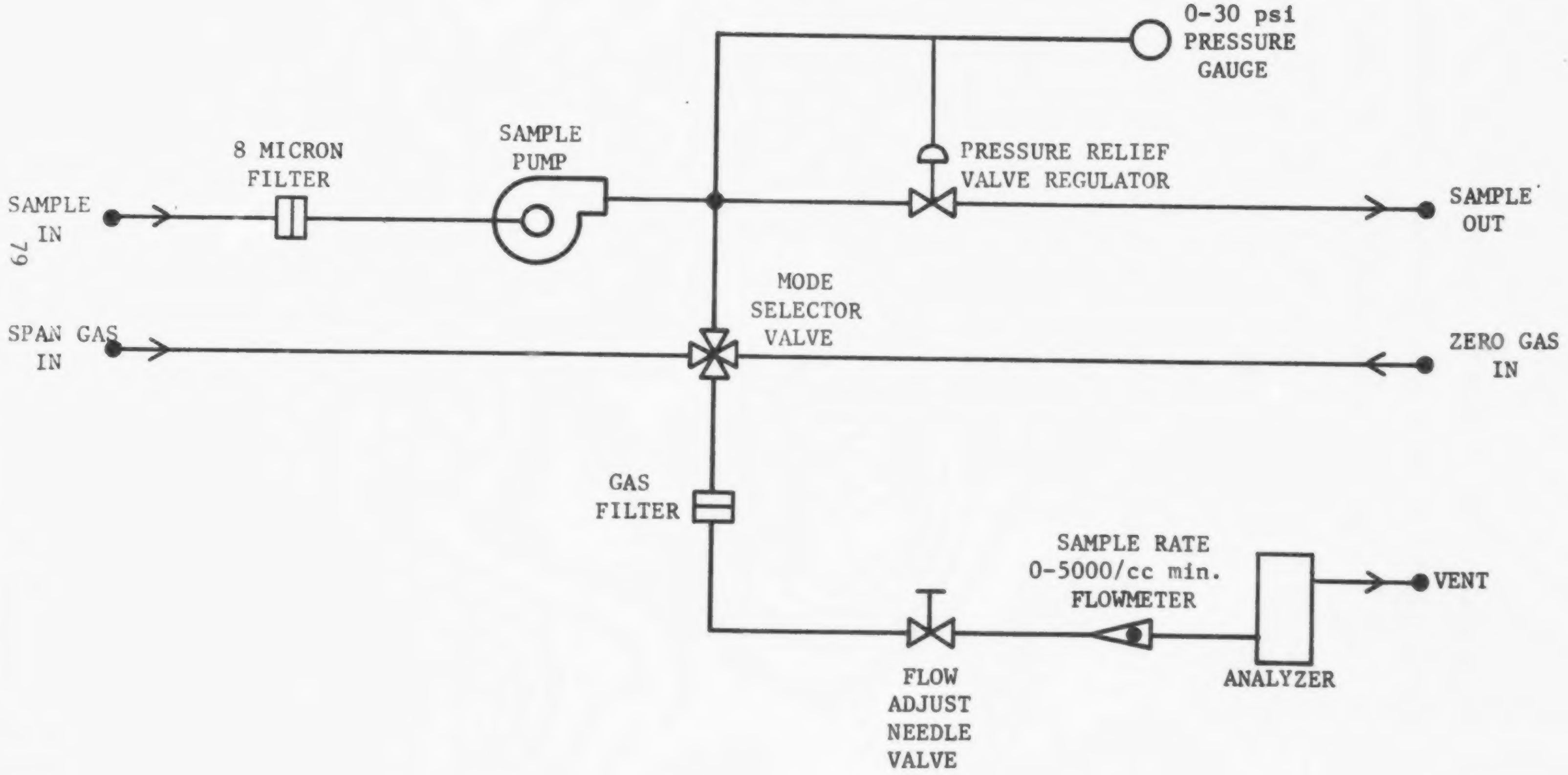

0-30 psi
PRESSURE
GAUGE
8 MICRON
FILTER
SAMPLE
PUMP
PRESSURE RELIEF
VALVE REGULATOR
SAMPLE
IN
SAMPLE
OUT
MODE
SELECTOR
VALVE
SPAN GAS
IN
ZERO GAS
IN
GAS
FILTER
SAMPLE RATE
0-5000/cc min.
FLOWMETER
VENT
ANALYZER
FLOW
ADJUST
NEEDLE
VALVE

Figure 4.22: Infrared Gas Analyzer Flow Diagram

(7) output: 0-10, 0-1000 MV, 0-1.0 volt;

(8) stated performance specifications (manufacturer)

   (a) minimum detectable sensitivity: 0.5 ppm;

   (b) linearity: ± 0.5% of full scale on 20, 50 ppm range,
   ± 1.0% of full scale on 25, 500,
   1000 ppm range;

   (c) noise: not specified;

   (d) precision: 1% full scale;

   (e) accuracy: not specified;

   (f) zero drift: 0.05% per hour or ± 1% per 24 hours,
   whichever is lower,
   ± 2% of full scale for 3 days;

   (g) span drift: 0.05% per hour or ± 1% per 24 hours,
   whichever is lower,
   ± 2% of full scale for 3 days;

   (h) operational period: 7 days

(9) required accessories: stripchart recorder.

4.11.2 Operational Summary

The carbon monoxide analyzer was installed in the mobile van on April 26, 1973 and operated continuously until July 31, 1973. During this period of time both short-term and long-term tests were performed on the analyzer in accordance with the test plan requirements. The frequency of performance monitoring during these tests was dependent on the particular requirements of the evaluation procedure being applied. Calibration frequency for short-term drift was on a daily basis, and that for longer term drift studies was on a weekly or biweekly basis.

During the three-month period in which the analyzer was operated and subjected to the performance evaluation tests, two failures occurred. One failure was attributed to a faulty diode resulting in blown fuses and the flexible coupling on chopper motor shaft dragging causing an erratic modulation frequency. A minimum amount of maintenance was required during this period of time. Routine maintenance involved replacement of the filter element on the sample inlet line.

4.12 ANDROS MODEL 7000 DUAL-ISOTOPE-FLUORESCENCE CARBON MONOXIDE ANALYZER

4.12.1 Instrument Description

The principle of operation of the Andros 7000 Dual-Isotope-Fluorescence NDIR analyzer is based on the ratio comparison of alternate infrared absorption of CO^{16} and CO^{18} radiation in a sample chamber. The IR radiation spectra that are an exact match of the vibrational-rotational absorption bands of CO^{16} and CO^{18} are produced and alternately allowed to enter the single sample chamber. The CO^{16} present in the sample chamber will absorb CO^{16} radiation but not CO^{18} radiation. The alternating CO^{16} and CO^{18} radiation levels are then converted to electrical signals by a solid-state IR detector. Ratio comparison of the two signals yields a voltage level corresponding to the CO-concentration in the sample air. A broad-band "blackbody" IR source is used to stimulate fluorescence of CO^{16} and CO^{18} isotopes contained in two sealed cells mounted on a rotating chopper wheel. Each cell, when appearing in the optical path, will filter, by absorption, either CO^{16} or CO^{18} IR radiation. The net result is a single beam of IR energy which consists of alternating CO^{16} and CO^{18} IR radiation. Particulate matter and moisture present in the gas under test or accumulated on the optical windows attenuates both IR pulses equally. Since 99.8% of all naturally occurring CO is CO^{16}, no ratio difference will be detected, thus eliminating drift problems associated with conventional NDIR analyzers using a separate reference chamber. A diagram of the D.I.F. analyzer is shown in Figure 4.23.

The physical characteristics and other descriptors of the Andros CO analyzer are as follows:

(1) overall dimensions: 19 in (48.3 cm) width,
5.25 in (13.3 cm) height,
16.75 in (42.5 cm) depth;

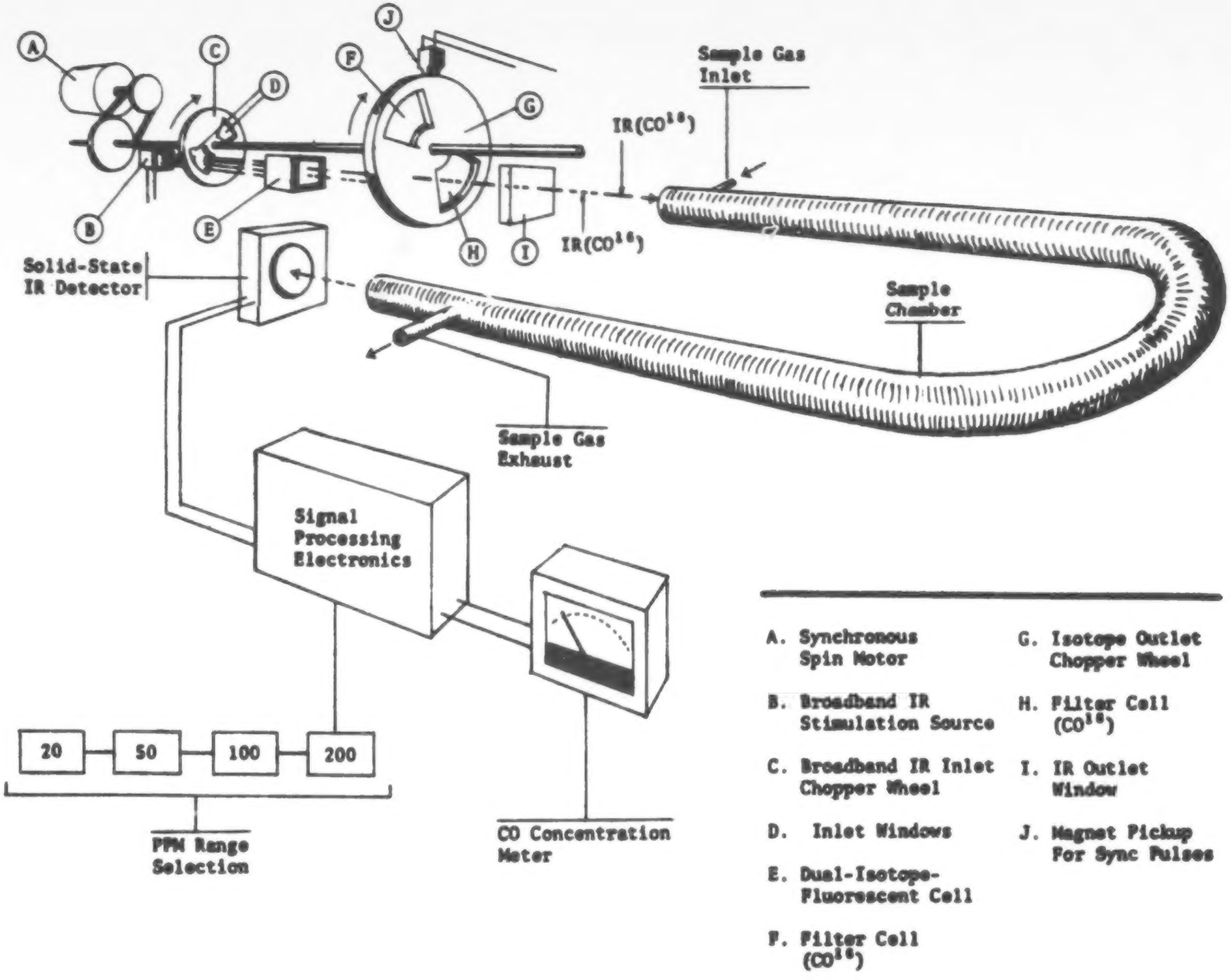

A
B
C
D
E
F
G
H
I
J
Sample Gas Inlet
IR(CO^{18})
IR(CO^{16})
Solid-State IR Detector
Sample Chamber
Sample Gas Exhaust
Signal Processing Electronics
20
50
100
200
PPM Range Selection
CO Concentration Meter
A. Synchronous Spin Motor
B. Broadband IR Stimulation Source
C. Broadband IR Inlet Chopper Wheel
D. Inlet Windows
E. Dual-Isotope-Fluorescent Cell
F. Filter Cell (CO^{16})
G. Isotope Outlet Chopper Wheel
H. Filter Cell (CO^{18})
I. IR Outlet Window
J. Magnet Pickup For Sync Pulses

Figure 4.23: Andros Carbon Monoxide Analyzer

The detector of the Andros 7000 uses a solid-state IR detector (photo-diode) which is mechanically rugged and non-microphonic. The detector is operated at peak CO-sensitivity by being thermally stabilized at -30°C by a Peltier Cooler. Since the detector is a solid-state device, high mechanical stability is achieved. The Andros analyzer is much less sensitive to shock and vibration than conventional NDIR analyzers.

4.12.2 Operational Summary

The dual-isotope-fluorescence NDIR analyzer was received from Andros and installed in the mobile van on March 22, 1973, but was found to be inoperative due to improper mounting of the pump prior to shipment. The pump was repaired, and the analyzer was set up on April 3, 1973 and operated continuously until May 25, 1973. During this period of time both short-term and long-term tests were performed on the analyzer in accordance with the test plan requirements. The frequency of performance monitoring during these tests was dependent on the particular requirements of the evaluation procedure being applied. Calibration frequency for short-term drift was on a daily basis, and that for longer term drift studies was on a weekly or biweekly basis.

During the approximately two-month period in which the analyzer was operated and subjected to the performance evaluation tests, two failures occurred, both as a result of power failures. Immediately upon resumption of AC power, the analyzer output was pegged off-scale on the 200-ppm scale when recording zero CO concentration for approximately 36 hours. Eventually the output signal decreased to a zero air value approximately 50% higher than the original zero level. After stabilization at that level, the proper zero level was reset using the zero adjustment control. This occurrence repeated itself on May 25, 1973, at which time the analyzer was returned to Andros for repairs.

4.13 TRACOR MODEL 270-HA GAS CHROMATOGRAPHIC-FLAME PHOTOMETRIC ANALYZER

4.13.1 Instrument Description

The principle of operation of the Tracor 270-HA analyzer is based on gas chromatographic separation of sulfur compounds (i.e., total sulfur, H_2S, and SO_2) and quantitative determination using a flame photometric detector equipped with a 394-nm optical filter. Low concentration levels (i.e., parts per billion) of total sulfur, H_2S, and SO_2 in ambient air can be quantitatively separated and measured. A typical chromatogram of a mixture of these sulfur compounds requires five minutes. A precolumn and backflushing are employed to prevent mercaptans from entering the analytical column. The system utilizes two sample loops, one for total sulfur and one for SO_2 and H_2S.

A schematic diagram is shown in Figure 4.24. Since a chromatographic column is used to quantitatively separate sulfur-containing compounds and since a 30,000-to-1 specificity ratio of sulfur to non-sulfur compounds is achieved by the detector, the GC-FPD measurement for H_2S and SO_2 is very specific. No interferences were observed from gases under study.

The basic components of the analyzer are a flame photometric detector, thermally stabilized oven housing for valves and columns, two-range signal linearizer, timing and control circuitry. The linearizer has two signal outputs for each pollutant. The low range is 0 to 0.1 ppm (0-261.8 $\mu g/m^3$) and the high range is 0.1 to 1.0 ppm (261.8-2618 $\mu g/m^3$).

The physical characteristics and other descriptors of the Tracor TS, H_2S, SO_2 analyzer are as follows:

(1) overall dimensions: 19 in (48.2 cm) width,
9 in (22.8 cm) height,
24 in (61.0 cm) depth;

(2) weight: 55 pounds (25.2 Kg);

(3) power requirements: 250 watts;

(4) measurement ranges: 0.1, 1.0 ppm full scale;

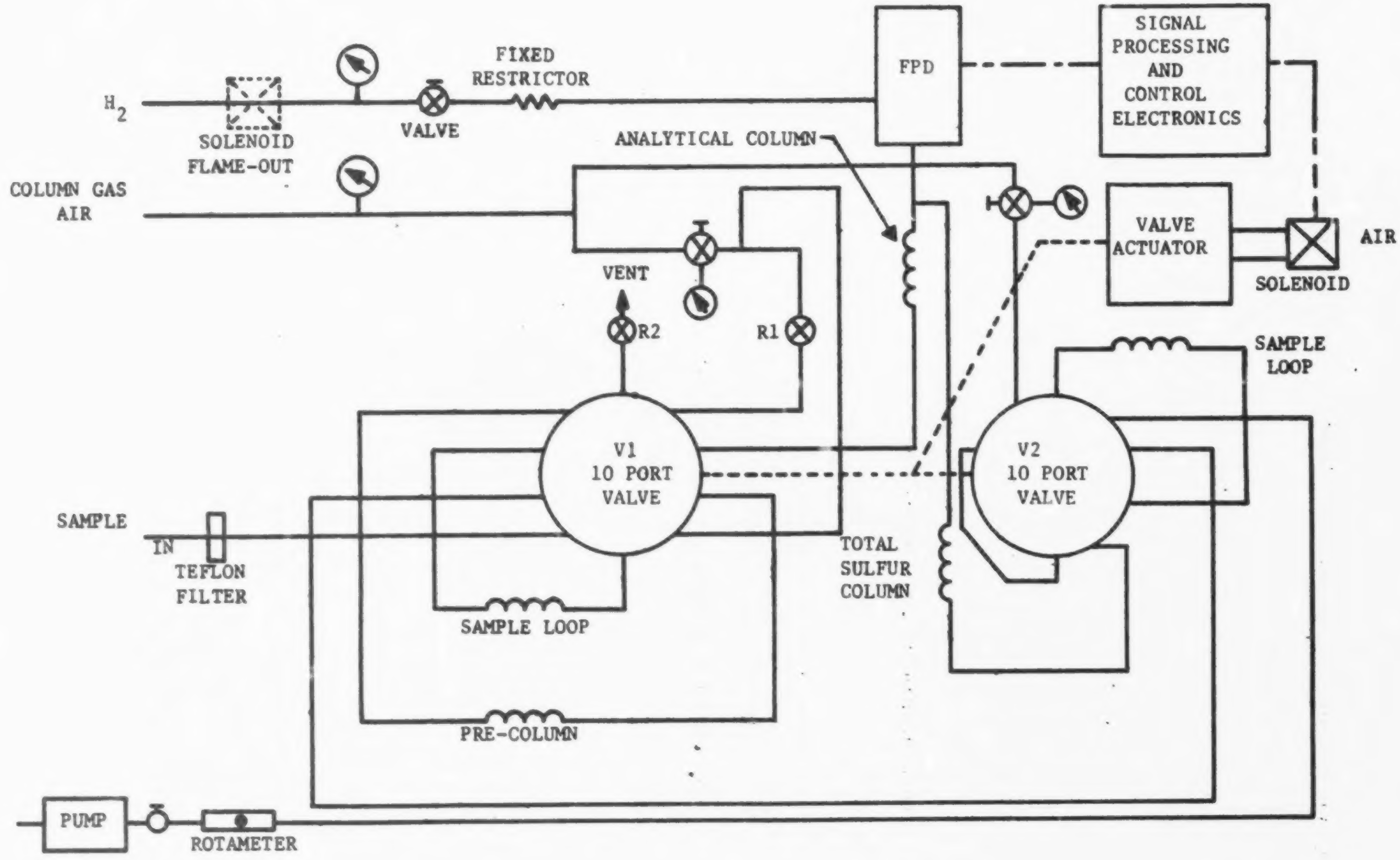

H2
SOLENOID
FLAME-OUT
VALVE
FIXED
RESTRICTOR
FPD
SIGNAL
PROCESSING
AND
CONTROL
ELECTRONICS
COLUMN GAS
AIR
ANALYTICAL COLUMN
VALVE
ACTUATOR
AIR
SOLENOID
VENT
R2
R1
SAMPLE
LOOP
V1
10 PORT
VALVE
V2
10 PORT
VALVE
SAMPLE
IN
TEFLON
FILTER
TOTAL
SULFUR
COLUMN
SAMPLE LOOP
PRE-COLUMN
PUMP
ROTAMETER

Figure 4.24: Schematic Diagram of Tracor Gas Chromatographic Flame Photometric TS, SO_2, H_2S Analyzer

(5) mode switch: inject/load sample (manual operation);

(6) cycle selector: automatic, manual and remote;

(7) output: trend and chromatograph, 0-1 volts DC

(8) stated performance specifications (manufacturer)

  (a) minimum detectable sensitivity: not specified;

  (b) linearity: not specified;

  (c) noise: not specified;

  (d) precision: not specified;

  (e) accuracy: not specified;

  (f) zero drift: not specified;

  (g) span drift: not specified;

  (h) operational period: not specified;

  (i) operating temperature: not specified;

(9) required accessories: cylinder H_2, air supply, two-stage regulator, stripchart recorder.

The gas flow system of the Tracor analyzer is composed of two 10-port valves, two sample loops, rotameter, flow control valve and pump. Sample flow rate is maintained at approximately 50 cc/minute by a variable restrictor and vacuum pump. Particulates greater than 5 microns in diameter are removed from the ambient air sample by a Teflon filter. The detector assembly of the analyzer consists of a flame chamber, optical filter, photomultiplier tube and housing. The basic functions of the photomultiplier assembly are to convert the low-level photons resulting from the excited sulfur atoms to electrical energy and to amplify the electrical signal for further processing through the high- or low-range linearizer, analog-to-digital converter, digital storage, and digital-to-analog converter output module circuitry. A block diagram of the detector and signal processing is shown in Figure 4.25.

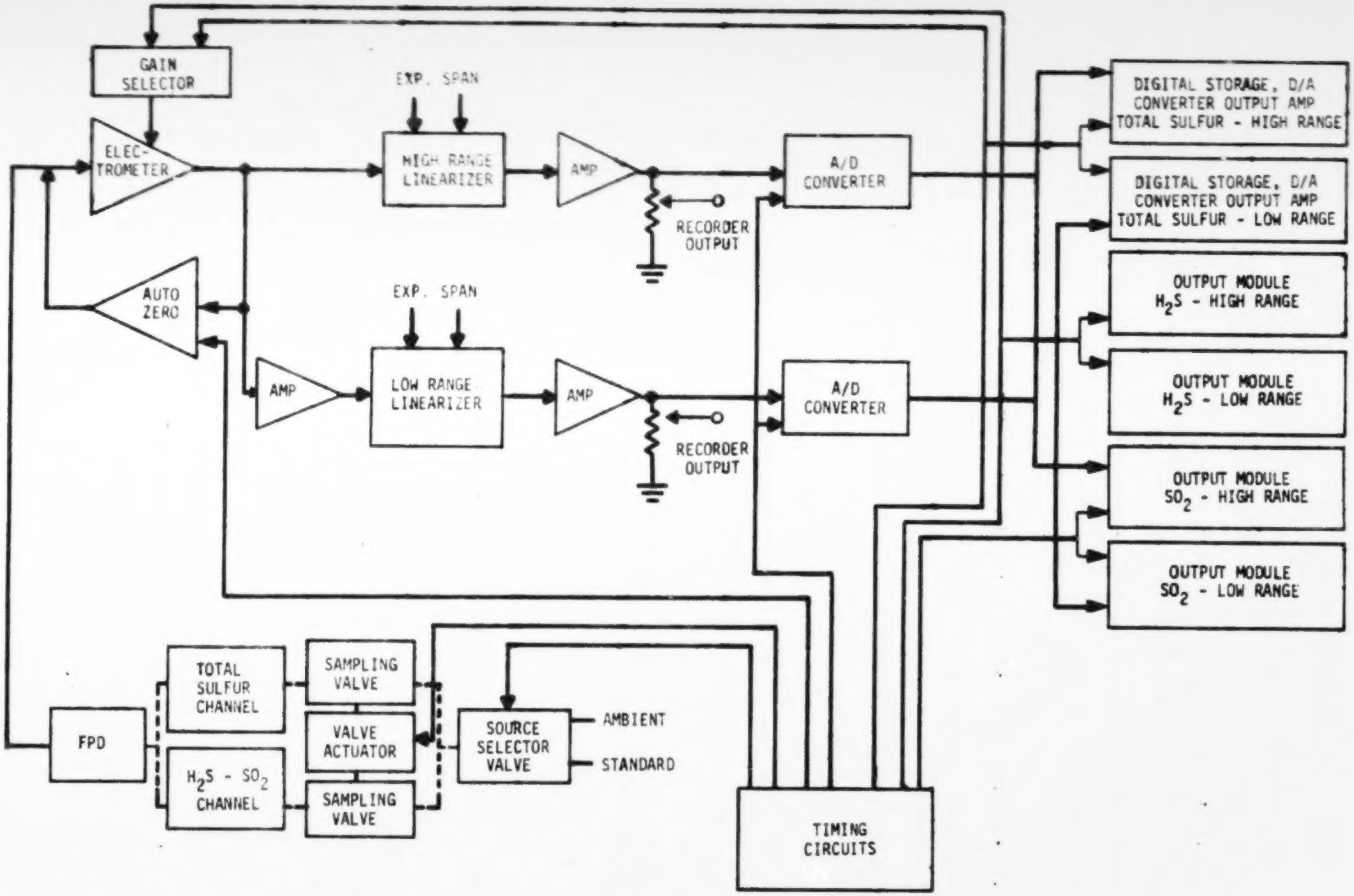

GAIN SELECTOR
EXP. SPAN
ELEC-TROMETER
HIGH RANGE LINEARIZER
AMP
A/D CONVERTER
RECORDER OUTPUT
DIGITAL STORAGE, D/A CONVERTER OUTPUT AMP TOTAL SULFUR - HIGH RANGE
DIGITAL STORAGE, D/A CONVERTER OUTPUT AMP TOTAL SULFUR - LOW RANGE
AUTO ZERO
EXP. SPAN
AMP
LOW RANGE LINEARIZER
AMP
A/D CONVERTER
RECORDER OUTPUT
OUTPUT MODULE H_2S - HIGH RANGE
OUTPUT MODULE H_2S - LOW RANGE
OUTPUT MODULE SO_2 - HIGH RANGE
OUTPUT MODULE SO_2 - LOW RANGE
TOTAL SULFUR CHANNEL
SAMPLING VALVE
VALVE ACTUATOR
SOURCE SELECTOR VALVE
AMBIENT
STANDARD
FPD
H_2S - SO_2 CHANNEL
SAMPLING VALVE
TIMING CIRCUITS

Figure 4.25: Block Diagram of Tracor Detector and Signal Processing

4.13.2 Operational Summary

The sulfur chromatograph was installed in the mobile van on December 18, 1972 and operated continuously until July 2, 1973. During this period of time both short-term and long-term tests were performed on the analyzer in accordance with the test plan requirements. The frequency of performance monitoring during these tests was dependent on the particular requirements of the evaluation procedure being applied. Calibration frequency for short-term drift was on a daily basis, and that for long-term drift studies was on a weekly or biweekly basis.

During the six-month period in which the analyzer was operated and subjected to the performance evaluation tests, five failures occurred, two involving vacuum pumps, and one each involving valve actuator, high range linearizer and total sulfur memory. A considerable amount of maintenance was required during this period of time. Routine maintenance involved replacing the Teflon filter element on the sample inlet line and changing compressed gas cylinders on a monthly basis.

4.14 BENDIX MODEL 8700 GAS CHROMATOGRAPH-FLAME PHOTOMETRIC ANALYZER

4.14.1 Instrument Description

The Bendix Environmental Chromatograph Model 8700 principle of operation is based on gas chromatographic separation of sulfur compounds (sulfur dioxide, hydrogen sulfide, and total sulfur) and quantitative determination using a flame photometric detector equipped with a 394-nm optical filter. The instrument consists of three sections: (1) control and signal processing electronics, (2) oven and analysis, and (3) sample system. The control electronics, timer, and electrometer are solid state and are mounted in a slideout drawer.

The electrometer output is linearized to provide an output signal directly proportional to the sulfur concentration. After the respective signals for each component have been linearized, they are stored in respective memories which are updated each cycle.

The analytical components are mounted in an insulated, temperature-controlled oven with associated valves and detector. The gas-handling system of the Bendix analyzer is composed of two 10-port valves, two sample loops, rotameter pressure regulators, and pump. The sample system includes a pump and associated flow control valves. The detector assembly of the analyzer consists of a flame chamber, optical filter, photomultiplier tube and housing. A schematic diagram is shown in Figure 4.26.

The physical characteristics and other descriptors of the Bendix chromatograph are as follows:

(1) overall dimensions: 22 in (56 cm) width,
41 in (104 cm) height,
23 in (58.5 cm) depth;

(2) weight: 250 pounds (113.6 Kg);

(3) power requirements: 800 watts, 115 Volt, 60 Hz;

(4) measurement range: 0.02 to 20 ppm on continuously adjustable attenuator for individual components

(5) outputs: 0-10 Volts trend-type for each component
10 MV chromatographic output

(6) stated performance specifications (manufacturer)

  (a) minimum detectable sensitivity: H_2S - 0.005 ppm
  SO_2 - 0.010 ppm
  TS - 0.010 ppm

  (b) linearity: less than 2% of full scale

  (c) noise: 0.5% of full scale

  (d) precision: ± 4% of full scale

  (e) accuracy: ± 2% of full scale

  (f) zero drift: less than ± 1% per day,
  2% per three days;
  automatic zero of baseline
  before each component;

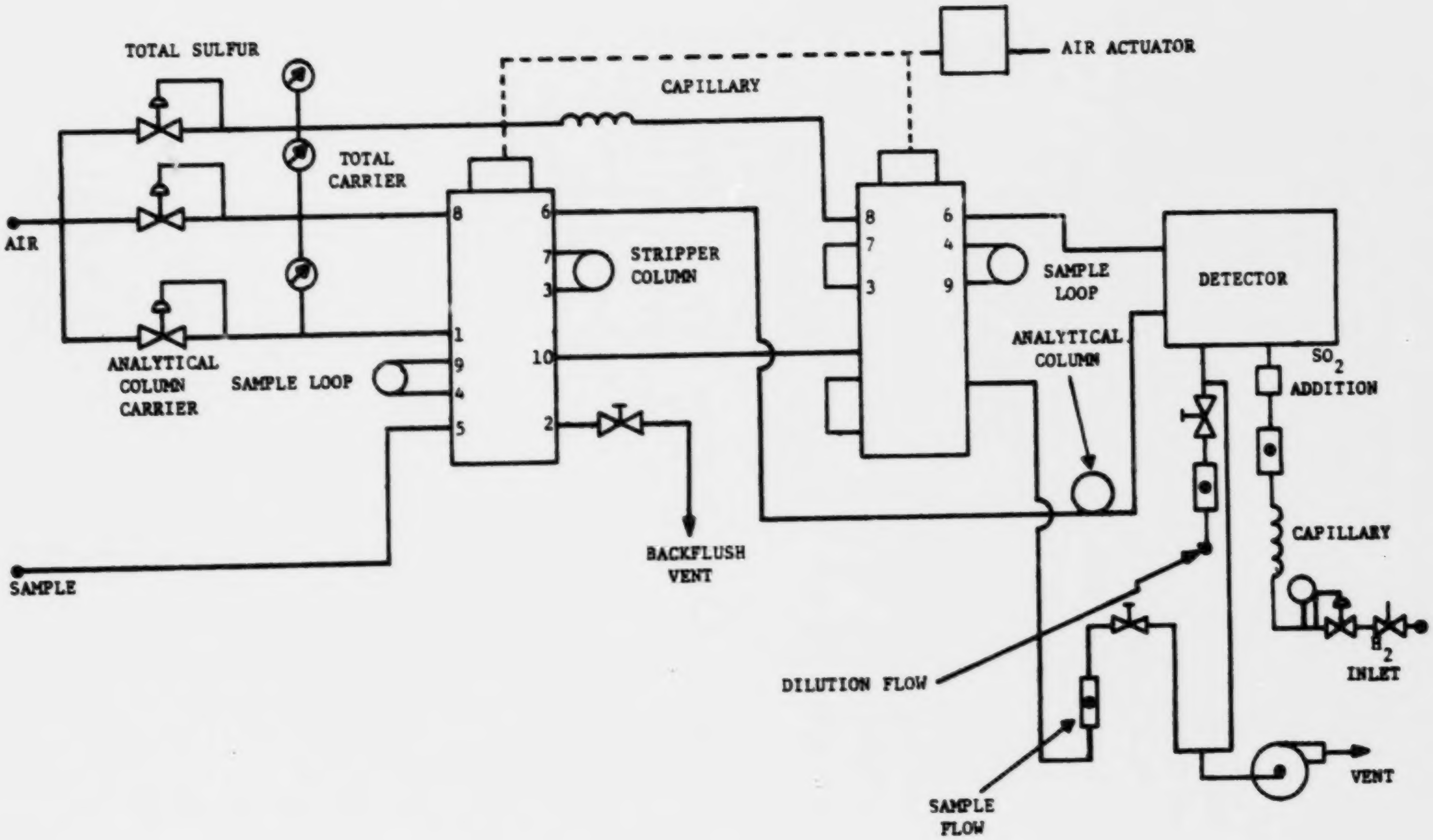

TOTAL SULFUR
AIR ACTUATOR
CAPILLARY
TOTAL CARRIER
AIR
8
6
7
3
STRIPPER COLUMN
1
9
4
5
10
2
ANALYTICAL COLUMN CARRIER
SAMPLE LOOP
8
7
3
6
4
9
SAMPLE LOOP
DETECTOR
ANALYTICAL COLUMN
SO_2 ADDITION
CAPILLARY
H_2 INLET
BACKFLUSH VENT
SAMPLE
DILUTION FLOW
SAMPLE FLOW
VENT

Figure 4.26: Bendix Model 8700 Chromatograph

(g) span drift: less than ± 1% per day,
2% per three days;

(h) operational period: more than three days
unattended;

4.14.2 Operational Summary

The sulfur chromatograph was installed in the mobile van on March 27, 1973 and operated continuously until July 3, 1973. During this period of time both short-term and long-term tests were performed on the analyzer in accordance with the test plan requirements. The frequency of performance monitoring during these tests was dependent on the particular requirements of the evaluation procedure being applied. Calibration frequency for short-term drift was on a daily basis, and that for long-term drift studies was on a weekly or biweekly basis.

During the three-month period in which the analyzer was available for evaluation, a minimum number of performance evaluation tests were performed due to time constraints; and no failure occurred. A minimum amount of maintenance was required during this period of time. Routine maintenance involved replacement of sample inlet filter element, maintaining hydrogen generator, and replacing compressed gases.

5.0 INSTRUMENT EVALUATION PROCEDURES

A general set of performance criteria was established in earlier reports describing field evaluation of advanced sensors for monitoring air pollutants[1,2,3]. These criteria were based on instrument characteristics that are independent of the type of instrument being evaluated or its application. Instrument performance characteristics fall into four major groups: physical characteristics, measured responses to standard test procedures, field data quality, and functional capacity. Physical characteristics are usually obvious and require minimal analysis. Response of instruments to standard test procedures poses no significant problems in determination of values for comparison with performance or desired operational specifications. Field data quality is concerned with calibration requirements, stability, accuracy, and limits of detection. Performance in the area of functional capacity is concerned primarily with instrument failure. The most obvious negative functional characteristics are instrument downtime and maintenance costs.

5.1 DEFINITIONS

The technical definitions used to describe sensor specifications for this program are as follows:

Range- - - - The minimum and maximum measurement limits which the instrument is capable of measuring.

Noise - - - Spontaneous, random, short-duration deviations in the instrument output about the mean output, which are not caused by input pollutant concentration changes.

Zero drift - The change in instrument output over a stated time period of unadjusted, continuous operation when the input concentration of pollutant is zero.

Span drift - The change in instrument output over a stated time period of unadjusted, continuous operation when the pollutant concentration is a stated value.

Linearity- - The standard deviation between the actual instrument reading and the reading predicted by the line of best fit as determined by the method of least squares.

Precision- - Variation about the mean of repeated measurements of the same concentration.

Minimum detectable concentration or limit - The smallest amount of input concentration which can be detected with a specified degree of confidence.

Lag time - - The time interval from a step change in the input concentration at the instrument inlet to the first corresponding change in the instrument output. This can be most reproducibly determined by extrapolating the slope at the 5% point.

Rise time- - The interval between the initial response time and the time to 95% response after a step change in the input concentration.

Fall time- - The interval between the lag time, t_1, and the time to 95% response after a step decrease in the inlet concentration. This time is not necessarily equal to the rise time in the instrument.

Line voltage - The RMS voltage supplied to the instrument.

Operational period - The period of time over which the instrument can be expected to give meaningful results without benefit of maintenance, service, or adjustment.

Accuracy - - The standard deviation between the indicated and the true values of the parameter being measured, unless otherwise stated. The true value is determined by analytical procedures consistent with the accepted reference methods.

5.2 TEST PROCEDURES

Test procedures were developed to determine the following parameters: stability, linearity, precision, minimum detectable concentration (sensitivity), response times (lag, rise, fall), noise, line voltage variation, and flow rate/pressure variation. The test procedures devised and utilized to determine each of these parameters are described in stepwise form in the following subcategories.

5.2.1 Stability - Zero and Span Drift

(1) Allow sufficient time for instrument to warm up and stabilize.

(2) Sample zero air until a stable reading is obtained and adjust baseline to 10% of chart. Instrument is operated at normal line voltage controlled at 117 volts. Normal room temperature is maintained at 25 ± 2°C.

(3) Sample test concentration of pollutant equal to 80 ± 5% of operating range selected. Adjust span control for appropriate reading.

(4) Generate and measure a test concentration equal to 20 ± 5% of the selected range. Do not adjust span control.

(5) At this point no adjustmants can be made to the instrument except in the case of failure or discontinuation of test. Instrument can sample ambient air or undergo other tests during idle periods.

(6) Generate and measure test pollutant concentrations of 0, 20, and 80% of the range limit each day, 24-hours after the previous day's readings. Test concentrations must be consistent from day to day. Allow sufficient time for stabilization of zero and span output and record data in concentration units. Subtract each day's readings from the previous day's respective readings to obtain zero and span drift for that day.

5.2.2 Linearity

(1) Allow sufficient time for instrument warm-up and stabilization.

(2) Sample zero air and adjust baseline to 10% of chart after stabilization period.

(3) Sample and measure at least eight different test concentrations evenly distributed on the operating range.

(4) Plot these test points, including zero, on a linear plot with test concentrations on the horizontal axis and instrument reading on the veritical axis. (See Figure 5.1.)

(5) Draw line of best fit determined by linear regression analysis.

(6) Calculate the standard deviations of the test points about the line of best fit.

5.2.3 Precision

(1) Allow sufficient time for instrument warm-up and stabilization.

(2) Sample and measure zero until a stable reading is obtained.

(3) Sample test concentration of 80% of range and record steady-state reading.

(4) Rapidly reduce pollutant concentration to zero air.

(5) Repeat Steps 3 and 4 six times and record each value.

(6) Calculate and report mean and standard deviations for this data.

5.2.4 Minimum Detectable Concentration (Limit)

(1) Allow sufficient time for instrument warm-up and stabilization.

(2) Run calibrations using a minimum of eight calibration standard, recording concentrations and instrument output.

5.2.2 Linearity

(1) Allow sufficient time for instrument warm-up and stabilization.

(2) Sample zero air and adjust baseline to 10% of chart after stabilization period.

(3) Sample and measure at least eight different test concentrations evenly distributed on the operating range.

(4) Plot these test points, including zero, on a linear plot with test concentrations on the horizontal axis and instrument reading on the veritical axis. (See Figure 5.1.)

(5) Draw line of best fit determined by linear regression analysis.

(6) Calculate the standard deviations of the test points about the line of best fit.

5.2.3 Precision

(1) Allow sufficient time for instrument warm-up and stabilization.

(2) Sample and measure zero until a stable reading is obtained.

(3) Sample test concentration of 80% of range and record steady-state reading.

(4) Rapidly reduce pollutant concentration to zero air.

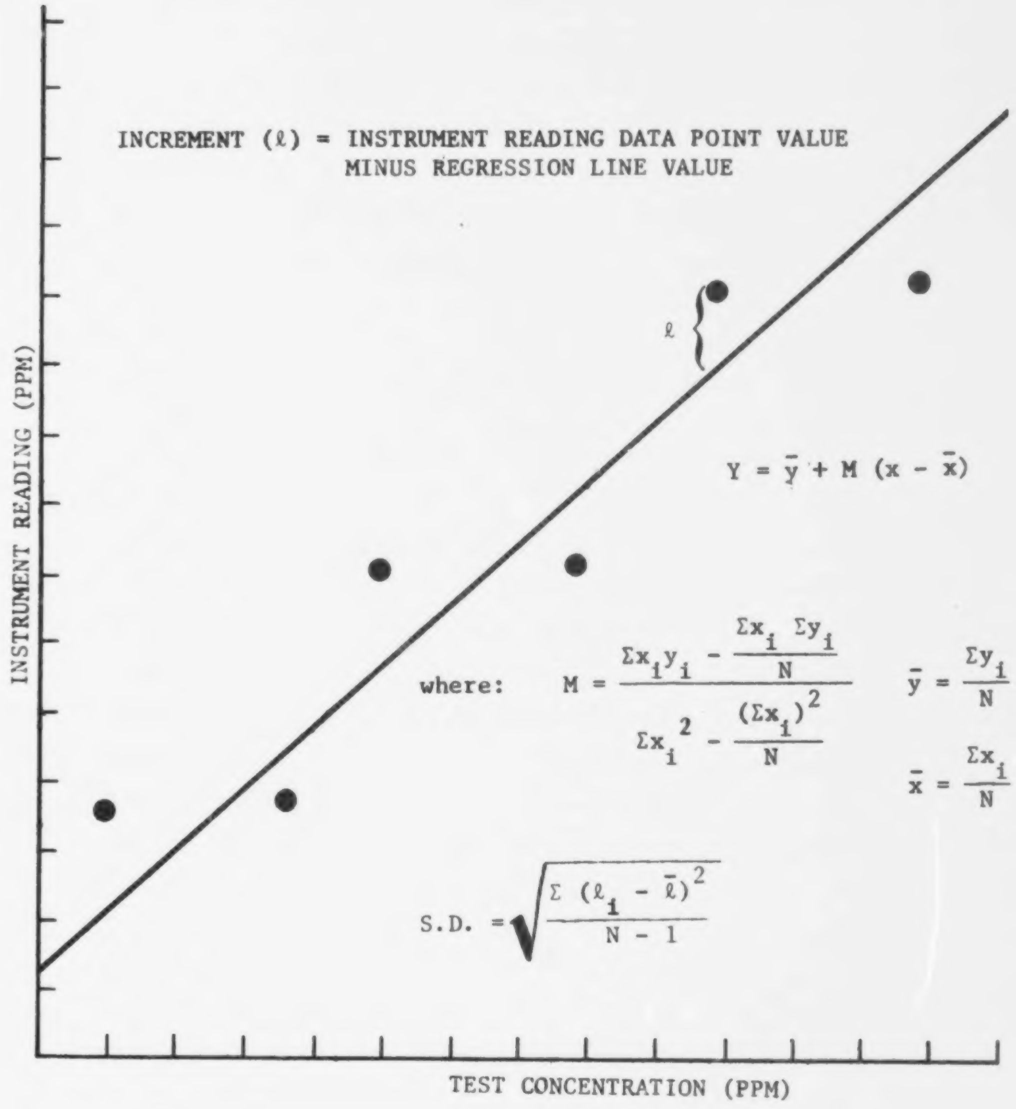
(5) Repeat Steps 3 and 4 six times and record each value.

(6) Calculate and report mean and standard deviations for this data.

5.2.4 Minimum Detectable Concentration (Limit)

(1) Allow sufficient time for instrument warm-up and stabilization.

(2) Run calibrations using a minimum of eight calibration standard, recording concentrations and instrument output.



INCREMENT (ℓ) = INSTRUMENT READING DATA POINT VALUE MINUS REGRESSION LINE VALUE

$$Y = \bar{y} + M\,(x - \bar{x})$$

$$\text{where:} \quad M = \frac{\Sigma x_i y_i - \dfrac{\Sigma x_i \; \Sigma y_i}{N}}{\Sigma x_i^{\,2} - \dfrac{(\Sigma x_i)^2}{N}} \qquad \bar{y} = \frac{\Sigma y_i}{N} \qquad \bar{x} = \frac{\Sigma x_i}{N}$$

$$\text{S.D.} = \sqrt{\frac{\Sigma\,(\ell_i - \bar{\ell})^2}{N - 1}}$$

Figure 5.1: Method of Determining Linearity

(3) Range of calibration standards should be as follows:

O_3 - - 0.2 ppm
NO - - 0.5 ppm
NO_2 - - 0.5 ppm
SO_2 - - 0.2 ppm
H_2S - - 0.2 ppm
CO - - 10.0 ppm
THC - - 10.0 ppm
CH_4 - - 10.0 ppm

(4) Plot signal output and calibration standards on ordinate and abscissa, respectively.

(5) Using linear regression, calculate and plot best fit line $Y = \bar{y} + b\ (x - \bar{x})$ as shown in Figure 5.2.

(6) Determine from a confidence level to 90% the students' t value corresponding to N-2 degrees of freedom.

(7) Calculate the signal level, (y_c), from the following equation for x = o.

$$y_c = \bar{y} + b(x - \bar{x}) + st\sqrt{1 + \frac{1}{N} + \frac{(x - \bar{x})^2}{\Sigma(xi - \bar{x})^2}}$$

where

$$s = \sqrt{\frac{\Sigma(yi - Yi)^2}{N - 2}} .$$

(8) Calculate the minimum detectable level (X_D) from the following equation:

$$Y_c = \bar{y} + b(X_D - \bar{X}) - St\sqrt{1 + \frac{1}{N} + \frac{(X_D - \bar{X})}{\Sigma(xi - \bar{x})^2}}$$

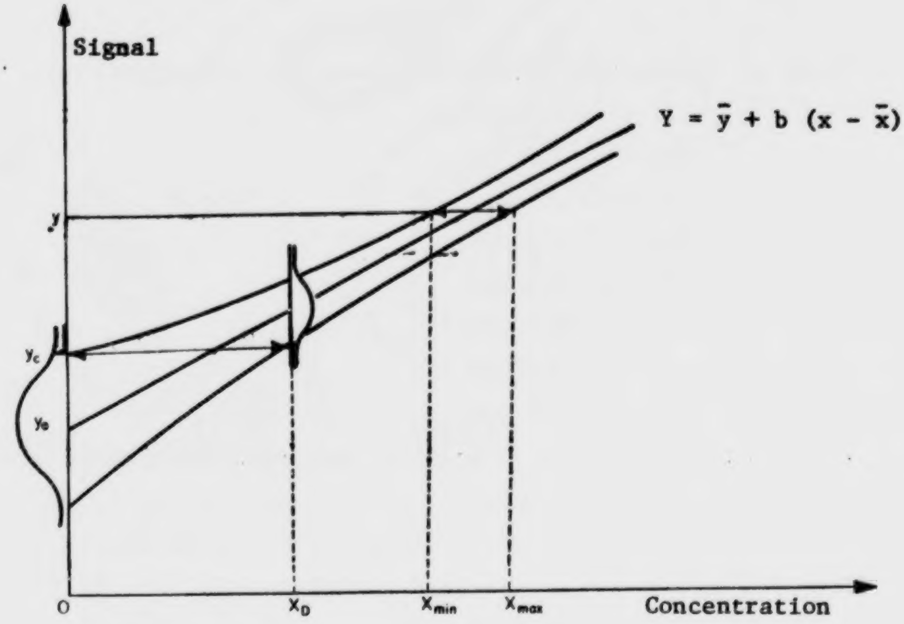


Figure 5.2. The Linear Calibration Line, With Its Upper and Lower Confidence Limits

5.2.5 Response Time

(Lag Time)

(1) Sample zero air until stabilized.

(2) Switch sample inlet to test concentration of 80% of operating range and simultaneously mark stripchart record.

(3) After instrument has stabilized, determine the 5% and 95% points of the stabilized final value.

(4) Draw a tangent line at the 5% point and note the zero intercept. Determine the time between the initial mark and the intercept to yield lag time.

(Rise Time)

(5) The rise is determined from the intercept to the 95% point.

(Fall Time)

(6) Sample at concentration of 80% of operating range and obtain a stable reading.

(7) Switch sample inlet to zero air and simultaneously mark stripchart recorder.

(8) Determine intercept using 5% (as in Step (4)) and 95% point. (See Figure 5.2.)

5.2.6 Noise

(1) Allow sufficient time for instrument warm-up using zero air.

(2) Connect instrument output to recording digital voltmeter sampling rate set at one-minute intervals.

(3) Sample zero air for 60 minutes.

(4) Locate the largest positive and negative excursions during the period and determine the maximum "peak-to-peak" value. Convert this value to concentration units.

(5) Repeat Steps (3) and (4) using a concentration of 80% of operating range.

(6) Record the maximum value in concentration units.

5.2.7 Line Voltage Variation

(1) Connect a variable transformer between the instrument and supply voltage. Allow the instrument to warm up with the variable transformer set at 117 volts.

(2) Calibrate the instrument using at least five concentration levels and determine the best fit line by regression analysis.

(3) Decrease line voltage to 105 volts and allow instrument to stabilize electrically and thermally.

(4) Repeat Step (2).

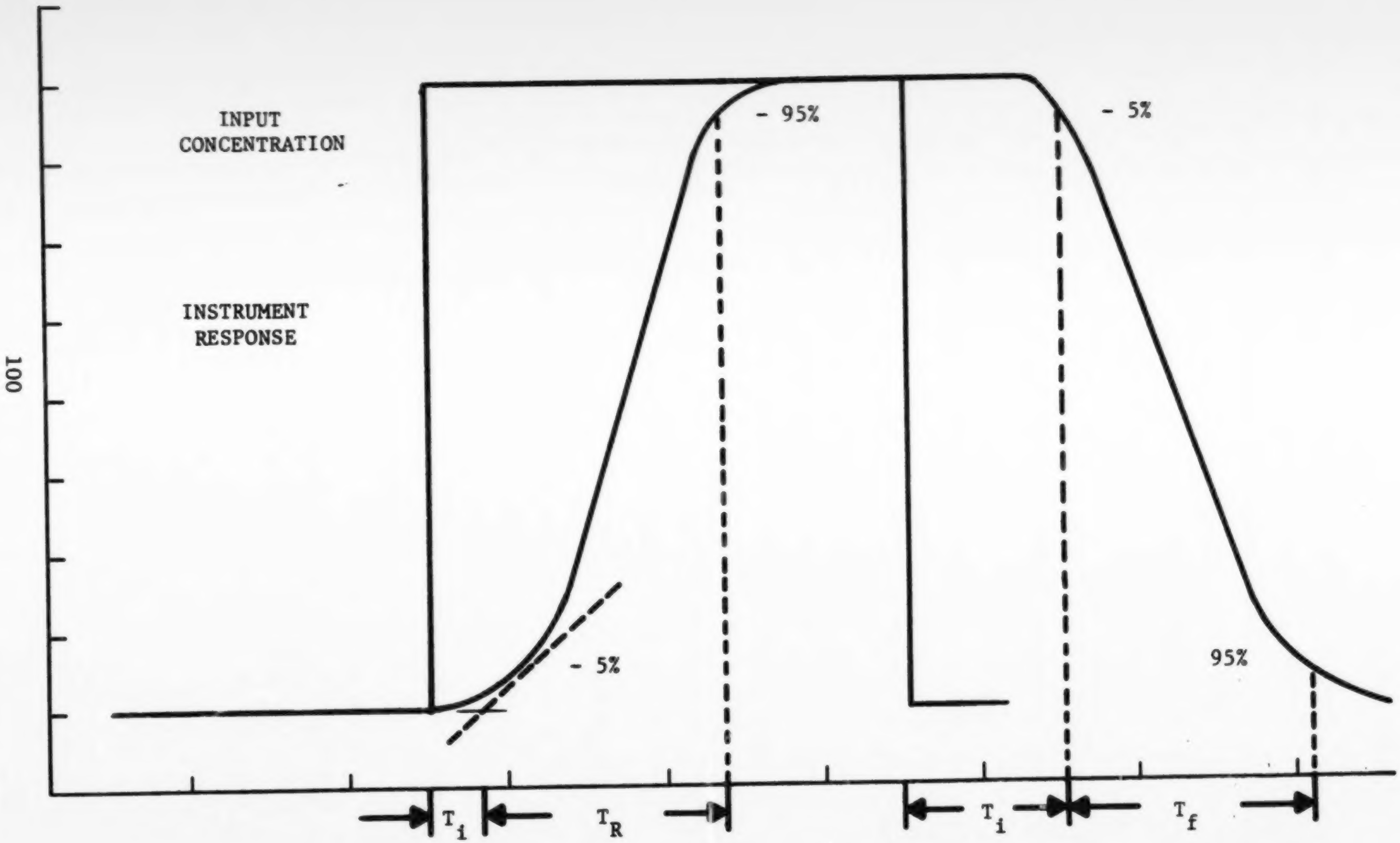

INPUT CONCENTRATION
INSTRUMENT RESPONSE
100
- 95%
- 5%
- 5%
95%
T_i
T_R
T_i
T_f

Figure 5.3: Instrument Response Time

(5) Increase line voltage to 125 volts and allow instrument to stabilize.

(6) Repeat Step (2).

(7) Calculate slope and intercept changes with respect to calibration data obtained at 117 volts.

5.2.8 Flow Rate/Pressure Variation

(1) Allow instrument to warm up and stabilize using a concentration level of 80% of the operating range.

(2) Adjust the flow rate or pressure up and down by a small increment (1-20% range) simulating a typical change preceding a failure for the instrument.

(3) Record instrument output for several pressure and/or flow rate increments to establish instrument response dependence.

(4) Express instrument response dependence as concentration units per pressure unit or concentration units per volumetric flow rate.

6.0 CALIBRATION SYSTEMS/PROCEDURES

6.1 CALIBRATION SYSTEMS

6.1.1 Ozone

A dynamic calibration system as described by Hodgeson *et al.*[12] and published with the National Primary and Secondary Ambient Air Quality Standards[13] was used to calibrate the ozone instrumentation evaluated during this study. Briefly, the ozone source consists of an 8-inch ultraviolet mercury lamp which irradiates a 5/8-inch quartz tube through which clean (compressed) air flows at 5 liters/minute. Ozone concentrations from 0 to approximately 1 ppm (1960 $\mu g/m^3$) can be generated by moving the shield and exposing various lengths of the lamp. Although the UV O_3 generator has been shown to be quite stable and reproducible[1,12], the neutral-buffered potassium iodide technique was used as the reference method[13]. A permanent calibration setup consisting of a zero air source, calibrated rotameter, UV generator, and a glass manifold was installed in the laboratory facility and calibrated by the manual neutral-buffered potassium iodide procedure periodically during the study. A diagram of the calibration system is shown in Figure 6.1.

6.1.2 Nitric Oxide/Nitrogen Dioxide

Due to problems associated with long-term use of NO_2 permeation tubes and the need to routinely determine the efficiency of the carbon, stainless steel, or molybdenum converters (which reduce NO_2 to NO), an alternate procedure (gas phase titration) was used for routine dynamic calibration of the chemiluminescent $NO\text{-}NO_x\text{-}NO_2$ analyzers. The gas phase titration technique is based upon application of the rapid gas phase reaction between NO and O_3 to produce a stoichiometric quantity of NO_2[7,8],

$$NO + O_3 \longrightarrow NO_2^* + O_2$$

$$NO_2^* \longrightarrow NO_2 + h\nu\ .$$

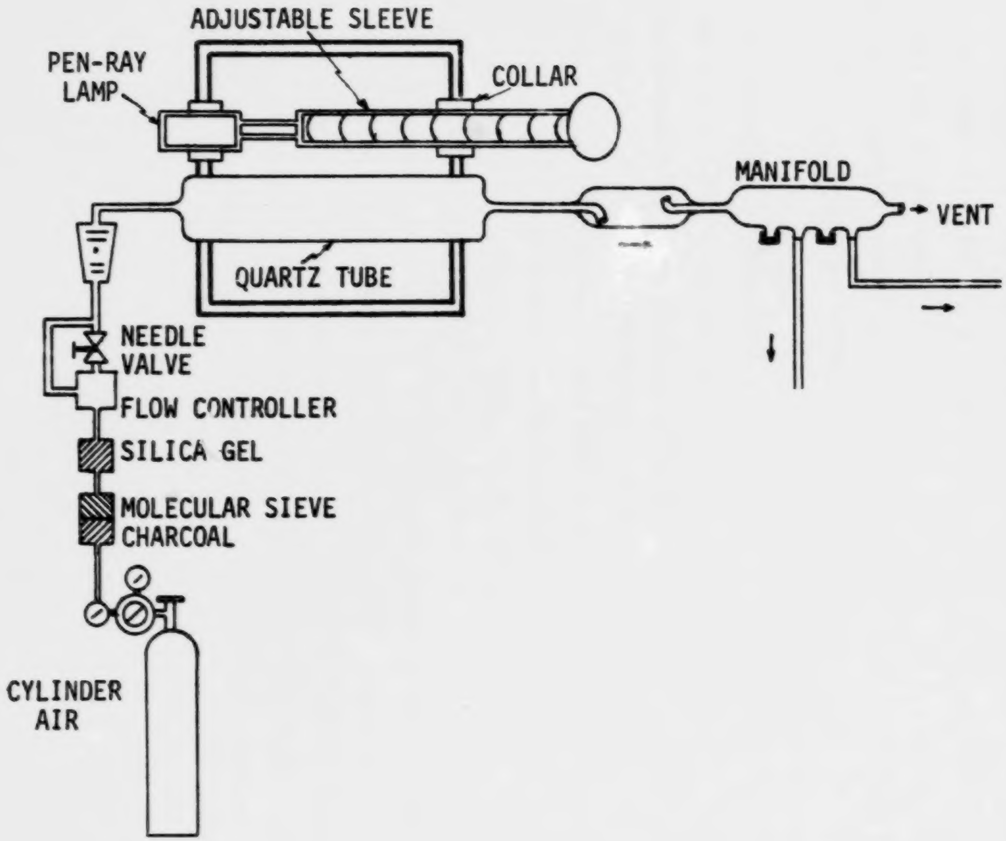

ADJUSTABLE SLEEVE
PEN-RAY LAMP
COLLAR
MANIFOLD
VENT
QUARTZ TUBE
NEEDLE VALVE
FLOW CONTROLLER
SILICA GEL
MOLECULAR SIEVE
CHARCOAL
CYLINDER AIR

Figure 6.1: Ozone Generation System for Calibrating Ozone Analyzers

Nitric oxide from a cylinder of NO in N_2 (100 ppm) is diluted with a constant flow of clean air to provide 1.0 ppm and used to calibrate the NO and NO_x cycles of the chemiluminescent NO-NO_x-NO_2 analyzer. By incorporation of a calibrated ozone generator in the calibration apparatus upstream from the point of NO addition, precise NO_2 concentrations can be generated by oxidation of NO to NO_2 with O_3. A schematic diagram showing the component parts of the calibration system is presented in Figure 6.2. As long as a slight excess of NO is present, the concentration of O_3 added is equivalent to the concentration of NO consumed and is equivalent to the concentration of NO_2 generated.

A general description of this calibration scheme is presented in the following paragraphs. Primary calibration of the NO concentration in the pressurized cylinder containing nitrogen as a diluent is accomplished by titration of an NO concentration of 1.0 ppm produced by dilution with successive concentrations of ozone (0-0.8 ppm) generated by an ozone generator which has been referenced to the neutral-buffered KI procedure[13]. The resultant NO detector outputs after stabilization at each titration point (i.e., 0.0, 0.1, 0.2, --- 0.8 ppm ozone added) are plotted in ppm on coordinate graph paper (y-axis) versus O_3 concentrations added, ppm (x-axis). A straight line is drawn through the linear portion of the titration curve and extrapolated to the x-axis. The concentration at the x-axis intercept, C_O', is the O_3 concentration equivalent to the initial diluted NO concentration. An example of a typical gas phase titration curve is presented in Figure 6.3. The concentration of NO in the cylinder can then be determined as follows:

$$C_{NO} = \frac{F_O \times C_O'}{F_{NO}}$$

where

C_{NO} = cylinder NO concentration, ppm,
F_{NO} = measured NO flow, cc/min,
C_O' = equivalence point O_3 concentration, ppm,
F_O = total clean air flow, cc/min.

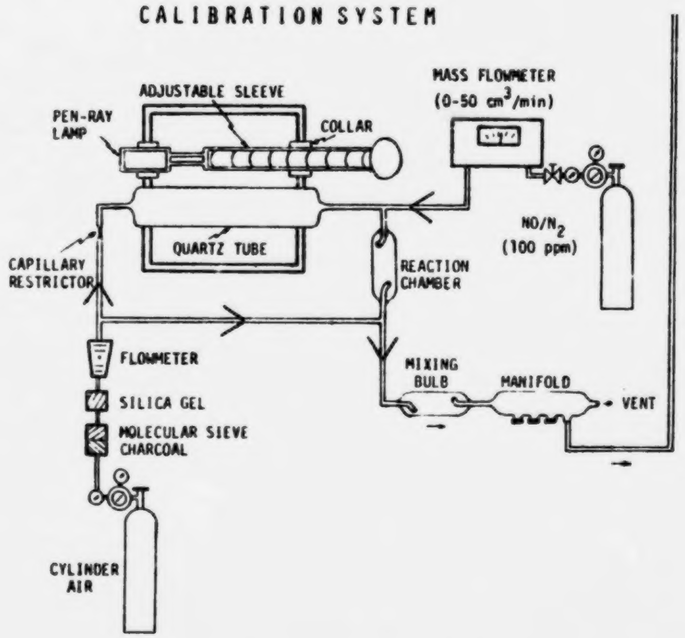

CALIBRATION SYSTEM
ADJUSTABLE SLEEVE
PEN-RAY LAMP
COLLAR
MASS FLOWMETER (0-50 cm^3/min)
NO/N$_2$ (100 ppm)
QUARTZ TUBE
CAPILLARY RESTRICTOR
REACTION CHAMBER
FLOWMETER
SILICA GEL
MOLECULAR SIEVE CHARCOAL
MIXING BULB
MANIFOLD
VENT
CYLINDER AIR

Figure 6.2: Gas Phase Titration System for Calibrating NO-NO$_x$-NO$_2$ Analyzers

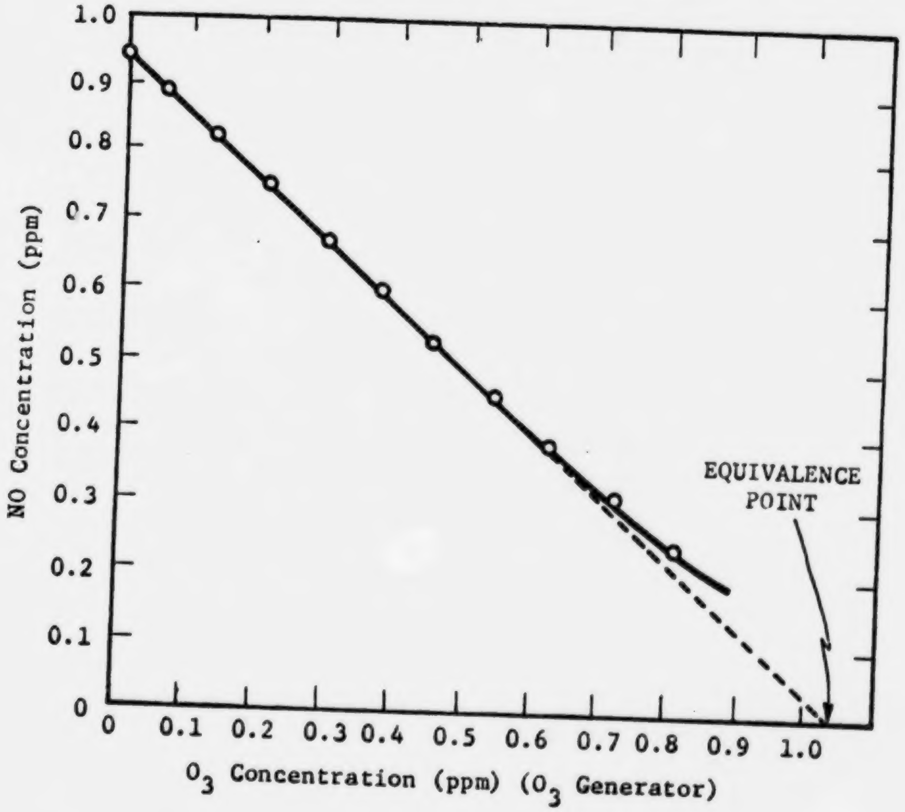


Figure 6.3: Gas-phase Titration of NO with O_3

Once the NO concentration in the cylinder has been determined, this cylinder can be used over its lifetime to provide a working standard for routine calibration[14]; however, to assure validity of data, the NO concentration should be verified at one-month intervals.

During routine calibration, the NO and NO_x channels of the chemiluminescent $NO-NO_x-NO_2$ analyzers were calibrated by dynamic flow dilution of the NO in nitrogen cylinder gas. To calibrate the NO_2 output channel and to determine the converter efficiency (i.e., efficiency of reduction of NO_2 to NO), a constant concentration of 0.5 or 1.0 ppm of NO is produced in the flow system. Ozone is then added in increments from the variable O_3 source. The incremental decrease of the NO measurement is then equivalent to the concentration of NO_2 produced by the gas phase titration reaction. In this scheme the calibrated O_3 source becomes a calibrated NO_2 source when NO is present in excess.

6.1.3 Sulfur Dioxide/Hydrogen Sulfide

A dynamic calibration system using a gravimetrically calibrated sulfur dioxide (SO_2) permeation tube[15] as a primary standard and zero air as diluent was used to provide known concentrations of SO_2 for calibration of total sulfur and sulfur dioxide analyzers. Gravimetrically calibrated SO_2 permeation tubes were obtained from the National Bureau of Standards. Hydrogen sulfide (H_2S) permeation tubes were purchased from Metronics, Inc., gravimetrically calibrated at EPA on a Cahn balance, and used to provide known concentrations of H_2S for the gas chromatographic-flame photometric analyzers evaluated during this study. Figure 6.4 shows the permeation tube calibration system used for this investigation. The permeation tube was housed in a pyrex glass holder and immersed in a constant temperature bath which maintained the tube at a temperature of 20.3°C ± 0.1°C. Dry, compressed air, conditioned to the temperature of the bath and metered through a rotameter, was passed over the permeation tube and into a 1-inch O.D. glass manifold from which the analyzers were allowed to sample. This allowed for simultaneous calibration of SO_2 and H_2S analyzers. Two permeation tube holders were utilized in this study--one each for the SO_2

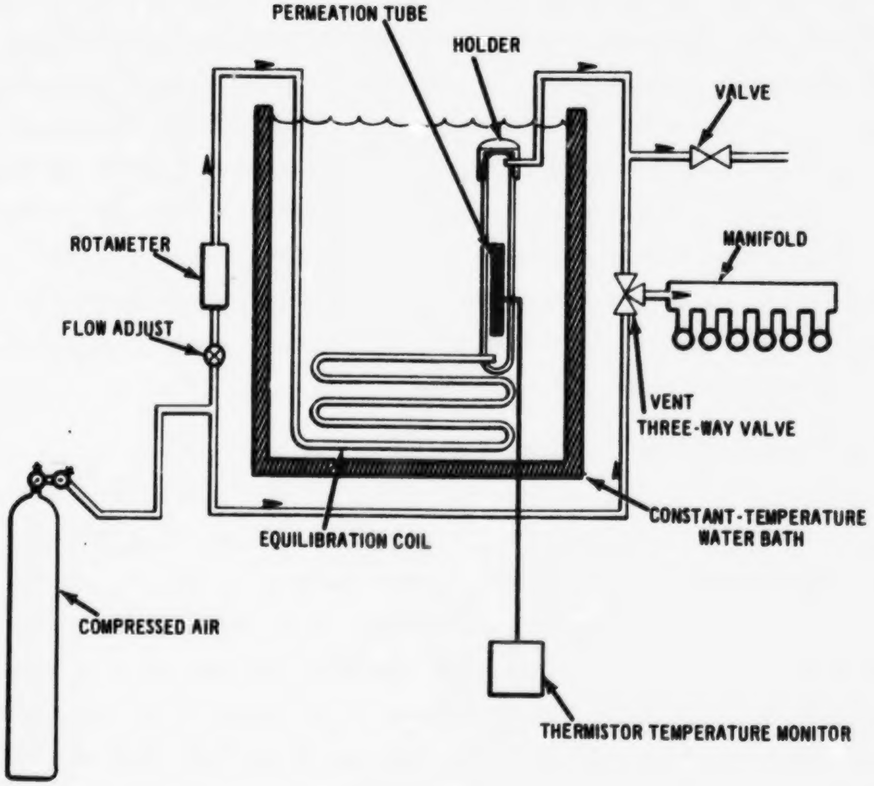

PERMEATION TUBE
HOLDER
VALVE
ROTAMETER
MANIFOLD
FLOW ADJUST
VENT
THREE-WAY VALVE
CONSTANT-TEMPERATURE WATER BATH
EQUILIBRATION COIL
COMPRESSED AIR
THERMISTOR TEMPERATURE MONITOR

Figure 6.4: Permeation Tube Calibration System

and H_2S tube. By varying diluent air flow rate, SO_2 or H_2S concentrations from 0 to 0.2 ppm (524 μg/m^3 SO_2, 279 μg/m^3 H_2S) could be generated and supplied to the respective analyzers during calibration.

6.1.4 Hydrocarbons/Carbon Monoxide

Calibration of hydrocarbon and carbon monoxide instruments was accomplished utilizing standard calibration gases certified by the supplier. For this study cylinders of methane and carbon monoxide in air were obtained from Scott Research Laboratories. Several concentrations ranging from 0 to 10 ppm of CH_4 and CO were used for calibration purposes. Cylinders of zero air (hydrocarbons $\leq$ 0.1 ppm) were supplied by several manufacturers for comparison purposes. The total hydrocarbon, methane, and carbon monoxide concentrations of each zero air cylinder were determined by analysis on a Beckman Model 6800 air quality chromatograph. The results of the analyses are as follows:

		Analysis Results		
Supplier	Certification by Manufacturer	THC (ppm)	CH_4 (ppm)	CO (ppm)
Matheson	THC as CH_4 <0.01 ppm	0.08	0.06	0.22
Scott Research Laboratories	THC < 0.1 ppm CO < 0.1 ppm	0.20	0.10	0.13
Linde	THC as CH_4 <0.1 ppm	0.18	0.08	0.63
Scientific Gas Products	THC as CH_4 <0.1 ppm CO < 1.0 ppm	0.20	0.08	0.67

The Matheson cylinder was utilized for zeroing the two hydrocarbon units evaluated during this investigation

6.2 CALIBRATION PROCEDURE

A general procedure applicable to the dynamic calibration of any analyzer was utilized in this investigation. Procedures and features developed during the previous Los Angeles Study[1] and in the St. Louis Study, Phase I and Phase II,[2,3] such as mode switch inputs describing instrument operational status and automatic entry of calibration data on magnetic tape were combined with on-line computer computation of transfer equations by linear regression analysis of calibration data and processing of air quality data in quasi real-time.

The basic step-wise procedure employed for dynamic calibration of all air quality analyzers was as follows:

(1) Verify operational status of each analyzer prior to beginning calibration.

(2) Connect instrument inlet line or instrument calibration inlet line, as the case may be, to the manifold of the calibration apparatus or for hydrocarbon and carbon monoxide instruments, directly to cylinders containing calibration gas.

(3) Allow instrument to sample zero air (i.e., air minus the pollutant of concern) for a period of time sufficient to establish a valid zero output. Indicate the proper manual entry status code zero and average the instrument output for zero input concentration for at least 15 minutes.

(4) Introduce a pollutant calibration concentration equal to approximately 80% of the operating range and adjust the span of instrument as required upon initial setup of the instrument. This adjustment is normally required only upon initial setup of an instrument or if excessive span drift occurred during the evaluation period. Minor adjustments in the span of each instrument can be performed by the on-line computer easier than by manual adjustment of the

span control knob, except for cases where drastic changes in span occurred. Omit Step (4) except on initial setup of analyzer.

(5) Introduce successive pollutant calibration concentrations of 10, 20, 40, 60, and 80% of the operating range of the instrument being calibrated. Allow sufficient time to establish a valid instrument output for each calibration concentration, and average the instrument output for that input calibration concentration for at least 15 minutes. Indicate the proper manual entry status codes for multipoint calibration and proceed to the next higher calibration concentration and repeat the sequence of events for multipoint calibration.

(6) Return the instrument inlet line to the ambient air sampling manifold and compute the transfer equation, which relates pollutant concentration input to instrument voltage output, for each instrument. This function was automatically computed at the end of each calibration by the on-line mini-computer employed during this instrument evaluation program.

The frequency of calibration performed during this investigation varied from daily to weekly to biweekly to monthly depending on the type of instrument being evaluated and on the type of test procedures being run. The frequency of calibration varied from daily to every other day when short-term zero and span drift was being determined, while the frequency of calibration might have been weekly for long-term drift (monthly basis). All calibration concentrations utilized in this investigation were generated using the apparatus and procedures described in the preceding section.

7.0 SUMMARY OF INSTRUMENT PERFORMANCE

7.1 EVALUATION TESTS

In determining performance specifications, it was of prime importance to recognize a properly operating instrument as opposed to a malfunctioning one. With new instrumentation, especially gas chromatographs, it was considered essential to have an experienced factory representative assist in the start-up and familiarization phase. This procedure was generally followed for most analyzers and aided in the assurance of a properly operating analyzer. During this evaluation several analyzers were returned to the manufacturers for repair and checkout prior to performance testing due to initial problems of instability, drifting, and erratic signal output.

Standard tests or those tests most widely accepted were used insofar as possible; however, for some performance characteristics (i.e., minimum detectable limit), existing test procedures are inadequate. Some test procedures, for example, recommend using test atmospheres equivalent to concentrations of two or three times the noise level. The accuracy with which test atmospheres of extremely low pollutant concentration can be generated at the present state-of-the-art is insufficient to evaluate minimum detectable limits. In this test procedure it was possible to statistically predict the minimum detectable limit more consistently than to determine the minimum detectable concentration by generating low concentration test atmospheres.

Most manufacturers' performance specifications tend to converge to the same value, typically 1 or 2% of full scale, for many performance factors. This indicates that performance specifications are more easily printed than demonstrated. Test procedures and statistical methods can influence results and cause resulting conclusions to deviate significantly from the manufacturer's specifications. Industry would do well to state and describe fully the test procedures used in performance testing.

7.1.1 Stability - Zero and Span Drift

The performance tests for stability were conducted as outlined in Section 5.2.1. The tests were conducted during a minimum time period of 12 days; however, long-term drift data were recorded intermittently during idle periods between tests or in conjunction with other tests that allowed unadjusted status of zero and span controls. The following data in Table 7.1 show zero and span drift, standard deviation and mean as percent of full scale from consecutive calibrations obtained on a daily basis except for week-ends and holidays.

Table 7.1. DRIFT TEST RESULTS

Instrument	Pollutant	Zero Drift/Week (%) Evaluation Test Result S.D.	Zero Drift/Week (%) Evaluation Test Result $\bar{X}$	Span Drift/Week (%) Evaluation Test Result S.D.	Span Drift/Week (%) Evaluation Test Result $\bar{X}$
Bendix 8002	O_3	0.1	0.03	3.0	-0.50
Dasibi 1003-AH	O_3	*	*	*	*
Bendix 8101-B	NO	0.4	0.05	1.1	-0.68
Bendix 8101-B	NO_2	0.4	-0.16	0.9	-0.62
Meloy 520	NO	1.5	0.68	6.9	2.80
Meloy 520	NO_2	.5	0.21	6.4	3.35
Rem 642	NO	*	*	*	*
Rem 642	NO_2	*	*	*	*
Thermo Electron 14	NO	0.3	-0.01	2.2	0.00
Thermo Electron 14	NO_2	0.2	0.06	2.5	-0.80
Bendix 8300	TS	5.0	1.82	10.7	4.18
Meloy SA-185R	TS	0.8	-0.04	2.5	-0.38
Tracor GC 270-HA	TS	0.3	0.00	9.2	-2.4
Tracor GC 270-HA	SO_2	0.2	-0.05	8.0	-2.3
Tracor GC 270-HA	H_2S	0.2	0.06	3.1	0.6
Andros 7000	CO	0.1	-0.16	1.4	-0.56
Bendix 8501-5FA	CO	0.4	1.56	1.0	0.14
Beckman GC 6800	CO	1.8	-0.42	3.1	0.78
Beckman GC 6800	THC	1.9	0.14	1.6	-0.24
Bendix GC 8201	THC	0.9	-0.27	2.4	1.27
Beckman GC 6800	CH_4	0.3	-0.04	1.9	0.96
Bendix GC 8201	CH_4	0.7	-0.35	1.7	0.88

S.D. - Standard Deviation
$\bar{X}$ - Mean
* - Not Available for Testing

7.1.2 Linearity

The linearity performance test was performed as outlined in Section 5.2.2. The data summary in Table 7.2 lists the standard deviation and mean value in concentration units of the vertical increments from data test points to the line of best-fit determined by linear regression analysis.

Table 7.2. LINEARITY TEST RESULTS

Instrument	Pollutant	Standard Deviation (ppm)	Mean (ppm)
Bendix 8002	O_3	0.00051	0.0000220
Dasibi 1003-AH	O_3	0.00075	0.0000310
Bendix 8101-B	NO	0.00890	0.0000510
Bendix 8101-B	NO_2	0.00100	-0.0001100
Meloy 520	NO	0.02700	-0.0056000
Meloy 520	NO_2	0.00620	0.0000052
Rem 642	NO	0.02800	-0.0000068
Rem 642	NO_2	0.01100	0.0000025
Thermo Electron 14	NO	0.00390	-0.0002000
Thermo Electron 14	NO_2	0.00330	0.0000077
Bendix 8300	TS	0.00430	-0.0003000
Meloy SA-185R	TS	0.00360	-0.0003000
Tracor GC 270-HA	TS	0.00428	0.0007500
Tracor GC 270-HA	SO_2	0.00448	0.0002000
Tracor GC 270-HA	H_2S	0.00099	0.0000000
Andros 7000	CO	0.32000	0.0038700
Beckman GC 6800	CO	0.01600	-0.0010700
Bendix 8501-5FA	CO	0.32900	0.1300000
Beckman GC 6800	THC	0.01800	0.0023000
Bendix GC 8201	THC	0.02100	0.0041000
Beckman GC 6800	CH_4	0.00585	-0.0002200
Bendix GC 8201	CH_4	0.01620	0.0032000

7.1.3 Precision

Precision performance tests were performed as outlined in Section 5.2.3. Precision is defined as the variation about the mean of repeated measurements of the same concentrations. The variation in Table 7.3 is expressed as one standard deviation about the mean which includes both instrument and calibration system errors.

Table 7.3. PRECISION TEST RESULTS

Instrument	Pollutant	Standard Deviation (ppm)	Mean (ppm)
Bendix 8002	O_3	0.0030	0.395
Dasibi 1003-AH	O_3	0.0040	0.357
Bendix 8101-B	NO	0.0030	0.403
Bendix 8101-B	NO_2	0.0021	0.401
Meloy 520	NO	0.0069	0.397
Meloy 520	NO_2	0.0073	0.405
Rem 642	NO	0.0150	0.388
Rem 642	NO_2	0.0040	0.400
Thermo Electron 14	NO	0.0029	0.404
Thermo Electron 14	NO_2	0.0056	0.408
Bendix 8300	TS	0.0110	0.135
Meloy 8A-185R	TS	0.0050	0.126
Tracor GC 270-HA	TS	0.0020	0.136
Tracor GC 270-HA	SO_2	0.0030	0.138
Tracor GC 270-HA	H_2S	0.0080	0.238
Andros 7000	CO	0.0460	4.190
Bendix 8501-5FA	CO	0.2040	9.710
Beckman GC 6800	CO	0.0680	9.830
Beckman GC 6800	THC	0.0120	2.340
Bendix GC 8201	THC	0.0330	4.220
Beckman GC 6800	CH_4	0.0100	2.160
Bendix GC 8201	CH_4	0.0360	4.270

7.1.4 Minimum Detectable Limit

The minimum detectable limit tests were performed as outlined in Section 5.2.4. The minimum detectable limit is dependent upon many of the other performance parameters. Both the test procedure and the method of evaluating test data will often reflect a dependency upon other performance factors in varying degrees. The method used in this evaluation is related to precision of the method, linearity, number of calibration points (8 to 10 points), range of operation, mode of partitioning the calibration points, mean value of the calibration concentrations (i.e., should be as low as practical), and replicate measurements performed on ambient samples.

The evaluation approach used in assessing the minimum detectable limit was conducted with the following guidelines:

(1) All analyzers would be tested for each pollutant on identical ranges, or as nearly so as feasible, being aware that a few instruments would undergo tests at ranges almost a decade higher than the most sensitive range;

(2) All analyzer signal outputs would behave linearly with pollutant concentration, and calibration data yield readily to linear regression analysis for a best-fit line;

(3) Output data would be converted to physical units (i.e., ppm or $\mu g/m^3$) using a transfer equation from the regression analysis;

(4) The appropriate operation and test range would be selected for measuring non-urban pollutant concentration levels for each pollutant; and

(5) The data acquisition system signal handling capability could function reliably with signal voltages less than 0.1 millivolt.

Analyzers measuring each pollutant underwent identical tests insofar as possible. Confidence levels of 90% and 60% were applied to all analyzers. This was satisfactory for O_3, NO, NO_2, SO_2, H_2S analyzers and respective calibration systems; however, hydrocarbon and carbon monoxide calibration standards tended to be the limiting factor in the evaluation. To alleviate this problem, standards were selected on a relative basis from an original lot of approximately 20 cylinders using data from all analyzers under test.

The minimum detectable limit for each analyzer in Table 7.4 should not be interpreted to mean that a particular analyzer cannot produce an

Table 7.4. MINIMUM DETECTABLE LIMIT TEST RESULTS

Instrument	Pollutant	Concentration (ppm) 90%	Concentration (ppm) 60%	Output Signal Level (90%) (Millivolts)
Bendix 8002	O_3	0.005	0.003	0.59
Dasibi 1003-AH	O_3	0.008	0.004	5.67
Bendix 8101-B	NO	0.031	0.016	17.10
Bendix 8101-B	NO_2	0.005	0.003	1.50
Meloy 520	NO	0.070	0.034	87.50
Meloy 520	NO_2	0.025	0.012	18.90
Rem 642	NO	0.118	0.059	94.40
Rem 642	NO_2	0.027	0.013	24.80
Thermo Electron 14	NO	0.016	0.008	1.25
Thermo Electron 14	NO_2	0.009	0.005	0.69
Bendix 8300	TS	0.008	0.004	0.41
Meloy SA-185R	TS	0.007	0.004	21.90
Tracor GC 270-HA	TS	0.016	0.008	56.80
Tracor GC 270-HA	SO_2	0.016	0.008	52.30
Tracor GC 270-HA	H_2S	0.006	0.003	13.40
Andros 7000	CO	0.740	0.370	2.56
Bendix 8501-5FA	CO	0.820	0.410	6.51
Beckman GC 6800	CO	0.120	0.060	72.90
Beckman GC 6800	THC	0.052	0.026	26.20
Bendix GC 8201	THC	0.082	0.041	38.30
Beckman GC 6800	CH_4	0.040	0.020	63.75
Bendix GC 8201	CH_4	0.140	0.070	63.79

observable response to a concentration level less than the minimum detectable limit as determined by these tests. It should be noted that some analyzers produced an observable response different from the zero reading for estimated concentrations levels in the range of 1/2 to 1/10 of the minimum detectable limit. These concentration levels were estimated by linear extrapolation of calibration data. Generation and transport of test atmospheres containing extremely low concentration levels are difficult to maintain with a significant degree of confidence. Tests were conducted using the Bendix NO_x, TS, and Tracor analyzers to determine the minimum concentration level that would yield a response different from the zero air measurement level. The analyzers were flushed with zero air and with low pollutant concentrations for one hour prior to attaining a stable reading. The test results for the Bendix NO_x, TS and Tracor SO_2 analyzers are shown as follows:

	Test Point #1			Test Point #2			Test Point #3		
	Conc.*	S.D.	Mean	Conc.*	S.D.	Mean	Conc.*	S.D.	Mean
Bendix NO_x	0	1.0	0.4	3.1	1.2	4.6	6.1	1.3	5.1
Bendix TS	0	0.6	1.6	13.5	1.1	4.7	15.8	0.9	6.7
Tracor SO_2	0	0.02	1.5	13.5	3.7	2.6	39.5	1.0	8.6

0.005 ppm (NO) = 6.12 $\mu g/m^3$ 0.010 ppm (SO_2) = 26.2 $\mu g/m^3$

* - Estimated Concentration ($\mu g/m^3$)

The mean values of the concentration levels are indicative of the non-zero pollutant levels; however, the large standard deviations exhibited show considerable overlapping of the analyzer readings.

7.1.5 Response (Lag, Rise, Fall time)

The response times were determined using the procedure outlined in Section 5.2.5. This procedure is applicable only for continuous analyzers. For semi-continuous analyzers, such as NO_2 instruments and gas chromatographs, the cycle time is reported as lag time. Response time test results are shown in Table 7.5.

Table 7.5. RESPONSE TIME TEST RESULTS

Instrument	Pollutant	Lag (sec)	Rise (sec)	Fall (sec)	Remarks
Bendix 8002	O_3	4.8	10.2	10.2	
Dasibi 1003-AH	O_3	20.0	--	--	Cycle Period
Bendix 8101-B	NO	5.0	15.0		NO Only
Bendix 8101-B	NO_2	60.0	--	--	Cycle Period
Meloy 520	NO	10.0	15.0	15.0	NO Only
Meloy 520	NO_2	25.0	--	--	Cycle Period
Rem 642	NO	6.0	9.0	9.0	NO Only
Rem 642	NO_2		--	--	Cycle Period
Thermo Electron 14	NO	5.0	10.0	10.2	NO, NO_x Only
Thermo Electron 14	NO_2	110.0	--	--	Cycle Period
Bendix 8300	TS	4.5	30.0	6.0	
Meloy SA-185R	TS	3.0	20.0	20.0	
Bendix GC 8700	TS	300.0	--	--	Cycle Period
Bendix GC 8700	SO_2	300.0	--	--	Cycle Period
Bendix GC 8700	H_2S	300.0	--	--	Cycle Period
Tracor GC 270-HA	TS	225.0	--	--	Cycle Period
Tracor GC 270-HA	SO_2	225.0	--	--	Cycle Period
Tracor GC 270-HA	H_2S	225.0	--	--	Cycle Period
Andros 7000	CO	5.0	22.0	22.0	
Bendix 8501-5FA	CO	39.8	85.0	85.0	
Beckman GC 6800	CO	300.0	--	--	Cycle Period
Beckman GC 6800	THC	300.0	--	--	Cycle Period
Beckman GC 6800	CH_4	300.0	--	--	Cycle Period
Bendix GC 8201	THC	215.0	--	--	Cycle Period
Bendix GC 8201	CH_4	215.0	--	--	Cycle Period

7.1.6 Noise

The performance tests for noise were conducted as outlined in Section 5.2.6. The noise tests were performed while the analyzers operated in their normal mode of operation. The oxides of nitrogen analyzers were operated in cyclic mode (i.e., periodically yielding NO_2 data). In this mode of operation the signals receive considerable integration before being stored in the memory circuits. The output from the memory circuit may be free from noise; however, the analyzer may be very noisy when operated in continuous mode with the signal bypassing the integrator and memory circuits. With gas chromatographs, the chromatographic signal may be noisey but may not be readily seen after the peak is stored in memory. For this reason, noise tests were not performed on gas chromatographic analyzers. both hydrocarbon and sulfur units. Noise test results are shown in Table 7.6.

7.1.7 Line Voltage Variation

Line voltage variation tests were performed only on total sulfur and oxides of nitrogen analyzers as outlined in Section 5.2.7. Each analyzer subjected to the test was initially operated and calibrated at a regulated line voltage of 117 volts. Each analyzer was then operated at 105 and 125 volts for a 16-hour stabilization period at each level and recalibrated. The calibration curve of the analyzer was then observed for offset and slope changes.

Variation in line voltage from 105 to 125 volts had no measurable effect on zero baseline for either the Bendix or Meloy total sulfur analyzers. Span sensitivity for both analyzers appeared to increase approximately 1% between the low voltage level (105 volts) and the two higher levels (117 and 125 volts).

The Bendix and Thermo Electron $NO-NO_2-NO_x$ analyzers were operated on 105, 117, and 125 ac line voltages on consecutive days with a 16-hour equilibration period overnight. The test employed a three-point dynamic calibration at each of the line voltage settings. The calibration curve of the analyzer was observed for offset and slope changes. The maximum

Table 7.6. NOISE TEST RESULTS

Instrument	Pollutant	Mean Concentration (ppm)	Noise (ppm)
Bendix 8002	O_3	0.000	0.0002
		0.400	0.0003
Dasibi 1003-AH	O_3	0.000	0.0005
		0.400	0.003
Bendix 8101-B	NO	0.000	0.0005
		0.400	0.0005
Bendix 8101-B	NO_2	0.000	0.0005
		0.400	0.0020
Meloy 520	NO	0.000	0.0020
		0.400	0.0035
Meloy 520	NO_2	0.000	0.0050
		0.400	0.0090
Rem 642	NO	0.000	0.0060
		0.400	0.0100
Rem 642	NO_2	0.000	0.0020
		0.400	0.0070
Thermo Electron 14	NO	0.000	0.0005
		0.400	0.0005
Thermo Electron 14	NO_2	0.000	0.0005
		0.400	0.0005
Bendix 8300	TS	0.00025	0.0003
		0.2044	0.0016
Meloy SA-185R	TS	0.00025	0.0006
		0.2044	0.0022

slope change was less than 0.4% for each of the outputs (NO, NO_2, NO_x) but did appear to change proportionately with line voltage changes. The Meloy NO-NO_2-NO_x analyzer was tested under the same conditions as mentioned in the foregoing paragraph. Operation at 117 and 125 volts appeared to be typical performance; however, at 105 volts the zero immediately went negative, equivalent to 0.06 ppm, and no response was observed for NO or NO_2 concentrations of 0.1 and 0.4 ppm. The probable cause of the malfunction was failure of the ozonator to produce ozone required for the reaction. When operating at a normal line voltage of 117 volts, the analyzer responded properly. No voltage variation tests were performed on the Rem analyzer, since it was removed from the evaluation prior to this performance test.

Minor excursions or variations in line voltage (105 to 125 volts) appear to have an insigificant effect on the performance of most of the analyzers evaluated; however, for optimum performance the use of a voltage regulation system capable of maintaining line voltage at 117 ± 2 volts is recommended.

7.1.8 Sample Flow Rate Test

Sample flow rate tests were performed according to the test procedure described in Section 5.2.7 on two analyzers (i.e., Bendix and Meloy total sulfur analyzers). These analyzers were selected for this test, since dilution air is added to the exhaust stream from the detector and maintaining proper flow rates has presented problems in the past. Each analyzer was calibrated at the manufacturer's recommended flow rate of 200 cc/min, and the flow rate was adjusted ± 10% while sampling a test concentration of sulfur dioxide. Results of this test indicate a significant decrease in response with a 10% increase in flow rate for both analyzers. This condition is usually not observed with field use of analyzers, in that flow rate normally decreases with time. Decreasing the flow rate by 10% had a much greater effect on the Bendix analyzer than it did on the Meloy. The minor difference in the indicated value of the calibration concentration for both analyzers at a flow rate of 200 cc/min can be attributed to analyzer drift between calibration and performance of the flow rate test.

Sample flow rate tests were not performed on several instruments due to the nature of their principle of operation or the flow system employed. Analyzers utilizing critical orifices to regulate or maintain a constant flow rate normally do not experience flow problems. The exception to this occurs when the orifice is plugged with particulate or the vacuum pump fails to maintain the proper pressure drop across the orifice. All chemiluminescent NO-NO_x-NO_2 analyzers, with the exception of the Rem unit, operate with critical orifices and at high vacuum within the reaction chamber. Variations in cell pressure or vacuum of 10 to 20 cm of Hg would not affect the flow rate through the instrument but can and do affect significantly the sensitivity of the Bendix, Meloy, and Thermo Electron analyzers. Tests indicated that the response of these analyzers is directly proportional to cell pressure (absolute pressure) and that the response decreases approximately 10% per 2.54 cm of Hg decrease from normal operating pressure (i.e., absolute pressure). Sample flow rate test results are shown in Table 7.7.

Table 7.7. SAMPLE FLOW RATE TEST

Flow Rate (cc/min)	Meloy (TS) Concentration Reading (ppm)	Bendix (TS) Concentration Reading (ppm)
190	0.138	0.169
200	0.135	0.140
220	0.103	*

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*Instrument has very low response at flow rates exceeding 200 cc/min.

7.2 OPERATIONAL SUMMARY

Operational data are summarized in Table 7.8 for each analyzer evaluated during this program. Since individual analyzers were available for varying periods of time during the evaluation period, the significance of the data are somewhat questionable for comparison purposes. The Dasibi ozone analyzer, for instance, was available for one week of evaluation, whereas the Bendix ozone analyzer was operational for six months. Therefore, it would be unfair to try to compare percent operational time and failure rates for instruments with unequal evaluation periods. The data presented in Table 7.8 should be interpreted individually on the basis of percent operational time, failure rate, and type of failure. For this evaluation, operational time is divided into the following categories:

(1) percent operational time, and
(2) percent downtime.

Percent operational time includes all categories or operational status other than downtime, which includes routine maintenance, awaiting repair, or repair. This includes calibration, performance testing, special tests, and availability for ambient air monitoring when tests were not being performed.

It should also be pointed out that the data presented in Table 7.8 are results of an evaluation of one unit assumed to be a fair representative of that particular model. Also, consideration should be given to the fact that most of the mechanical and electrical failures experienced are of the type that can be corrected by redesign or replacement of the component part and are not basic flaws in the measurement principle itself.

7.3 SUBSYSTEM COMPONENT EVALUATION/RECOMMENDED MODIFICATIONS TO IMPROVE PERFORMANCE

To meet the objectives of this program and adequately evaluate the performance of the analyzers under investigation, it was necessary to separate the analyzers into three subsystems, to look at the contribution of each subsystem to the total performance of the analyzer, to identify

Table 7.8. OPERATIONAL SUMMARY

Instrument	Operational Period (Days)	% Operational Time	% Downtime	Failures #	Nature of Failure
Bendix O_3	230	96.0	4.0	2	a, b
Dasibi O_3	7	100	0.0	0	
Bendix $NO-NO_x-NO_2$	175	94.5	5.5	2	c
Meloy $NO-NO_x-NO_2$	175	65.0	35.0	5	a, d, e
Thermo Electron $NO-NO_x-NO_2$	65	96.0	4.0	1	f
Rem $NO-NO_x-NO_2$	56	75.0	25.0	3	d, g
Bendix TS	138	97.0	3.0	1	g
Meloy TS	150	98.6	1.4	0	
Beckman ($THC-CH_4$)	214	90.0	10.0	2	h, i
Bendix ($THC-CH_4-NMHC$)	168	67.0	23.0	2	g, j
Beckman 6800 (CO)	214	90.0	10.0	2	h, i
Andros CO	50	90.0	10.0	2	g
Bendix CO	77	90.0	10.0	2	d, g
Tracor ($TS-H_2S-SO_2$)	202	80.0	20.0	5	c, g, j
Bendix ($TS-H_2S-SO_2$)	90	96.0	4.0	0	

a - detector cell failure (PM tube power supply)
b - flow rate instability
c - vacuum pump failure
d - engineering design/mechanical failure
e - ozonator transformer failure
f - converter heater failure
g - electronic circuitry failure
h - valve slider failure
i - oven temperature controller failure
j - valve actuator failure

weaknesses and general deficiencies in each subsystem, to recommend modifications and/or design changes to correct deficiencies whenever possible, and to document and report these findings. From the onset of this program, it was obvious that a thorough subsystem component evaluation was not within the scope of this work, due to time and money constraints. The optimum approach would be to divide each analyzer into three basic component subsystems (i.e., gas flow system, detector system, and signal processing system); to examine subjectively the components of each subsystem with special attention being given to anticipated effects on the total performance of the analyzer; to perform testing to validate subjective judgment on identifiable weaknesses and/or deficiencies in the design of a particular component and report test results to the Project Monitor and the respective manufacturer; to recommend or suggest engineering modifications or alternate approaches to upgrade the subsystem components; to document these findings; and to retest and evaluate the effect of the recommended design changes on instrument performance. Unfortunately, it was not possible to accomplish all these tasks within the specified time limits. In most cases all the objectives were completed with the exception of retesting each analyzer to evaluate the effect of modifications on instrument performance. Some recommended modifications were implemented immediately, and their effect on improvement of instrument performance is easily identifiable; others were completely ignored and never implemented or are being implemented at the present time.

To report in detail the results of the subsystem component evaluation would require several volumes. Therefore, a general description of the major component systems for each set of analyzers will be presented in the following sections, with attention being given to design consideration rather than simple component failure. Section 7.6 will present what is considered to be a composite list of general deficiencies encountered with the analyzers evaluated in this investigation. This list is segmented by subsystems (i.e., gas flow, detector, and signal processing), applies to some but not all the analyzers evaluated, and is not all inclusive.

7.3.1 Ozone Analyzers

Flow systems for ozone analyzers evaluated in this program can be classified into two groups: a chemiluminescent analyzer with both ethylene and sample flow rates and a UV-adsorption instrument with only sample flow. The sample flow rate of the Dasibi ozone analyzer may be set over a relatively wide range, typically 1 to 5 liters per minute, without introducing any measurement errors. The sample flow rate of the Bendix ozone analyzer must be accurately controlled to ensure calibration stability. An increase in sample flow rate increases the available ozone per unit time to react with the excess ethylene, yielding more chemiluminescence and, therefore, increased signal output. The ethylene flow rate was varied ± 10% of the nominal flow rate (25 cc per minute) without significantly affecting a given signal level of the analyzer. The ethylene and sample flow patterns within the detector cell are designed to minimize deposits on the optical window. This is accomplished with the ethylene and sample flows converging at right angles in a plane parallel to the optical window and exhausting opposite the PM tube cathode.

The Bendix analyzer has a chemical filter mounted on the rear of the cabinet for providing zero air. This filter is connected to the sample inlet line by a three-way, Teflon solenoid valve. The chemical filter contains molecular sieves, indicating silica gel, and charcoal, and with proper maintenance provides adequate zero air for the analyzer for routine checks.

The Dasibi analyzer flow path alternates the flow between the ozone catalyst (to provide zero air) and the ambient air during the measurement cycle. The analyzer is referenced to zero air in each cycle and automatically compensates for lamp intensity output irregularities throughout the cycle. The ozone catalyst is adequate for providing a reference sample for several months.

The detector systems utilized in both UV-adsorption and chemiluminescence analyzers appear to have adequate response and sensitivity. The high voltage power supply and the photomultiplier tube share a common thermostated housing. Power outages during the evaluation resulted in failure of the high voltage power supply. Although field repair of the detector cell is not recommended by the manufacturer, an accessible test point from the high voltage circuitry would facilitate fault isolation. No major deficiencies were observed with the UV-detector system.

The signal processing in the chemiluminescence analyzer uses an electrometer with a selectable time constant for filtering or smoothing the signal. The time constants available are 1, 10 and 40 seconds. The longer time constants are not essential to decrease noise of the analyzer to an acceptable level, but provide smoothing of the signal to aid in output sampling of instantaneous points by the data acquisition system.

The UV-adsorption analyzer measures the ambient sample and reference sample for two very short periods with respect to the cycle period. The ratio of the actual measurement period to cycle period is very small and may be undesirable where finely detailed data are required (i.e., response times less than 20 seconds).

7.3.2 Oxides of Nitrogen Analyzers

Flow systems for oxides of nitrogen analyzers evaluated during this study can be divided into two types with respect to vacuum pump location or reactor cell pressure. One type of analyzer utilizes the pump upstream from the detector cell and operates near ambient pressure; the other type employs the evacuation pump downstream from the reactor cell and, hence, has cell pressures of approximately 23 to 30 in (58.4 to 76.2 cm) of Hg. Each of the design considerations has its advantages and disadvantages, some of which are listed as follows:

Ambient Pressure Reactor (REM Analyzer)

Advantages	Disadvantages
(1) flow rate independent of ambient pressure changes or altitude	(1) larger sample required for existing detector design (i.e., 600 cc/min)
(2) no oxygen cylinder required for ozonator	(2) possible variable loss rate of sample in sample pump
	(3) desiccant change every 2 days due to moisture in the air flowing to ozonator

Low Pressure Reactor (Bendix, Meloy, Thermo Electron)

Advantages	Disadvantages
(1) small sample flow rate (100-200 cc/min)	(1) response dependent upon cell pressure (approximately 10% decrease per 2.54 cm of Hg decrease)
(2) small air or oxygen flow rate (50-100 cc/min) for ozonator	(2) desiccant change every ten days (high R.H.)

The use of air as a source of oxygen for the ozonator is satisfactory and stable, providing the desiccant is changed properly and timely. The replacement period is variable often by a factor of two (i.e., dry ambient, 20 day period, versus high relative humidity, 10 day period) and provides additional logistics for a monitoring site. The use of oxygen cylinders is also a logistical problem, but usually very infrequent, requiring replacement twice a year.

The pressure along sample flow paths employed by low reactor pressure analyzers varies significantly. In the Bendix analyzer low pressure is maintained from the pump, ozone scrubber, detector cell and to each of two capillaries used for flow control for ozone and sample. Therefore, a minimum number of fittings or connections are exposed under vacuum conditions. In the Thermo Electron analyzer low pressure is maintained from the vacuum pump, accumulator, reaction cell, catalytic converter, cycling solenoid valve, ozone capillary and sample capillary. The potential for development of leaks is about twice as great for the Thermo Electron as for the Bendix analyzer.

Converters may use many materials, such as molybdenum, stainless steel, carbon, and carbon-coated gold, for converting NO_2 to NO. Conversion efficiency is typically 93 to 100%. The molybdenum converter used with the Thermo Electron analyzer yielded the highest conversion efficiency lifetime, with the Bendix carbon unit, Meloy converter, and Rem molybdenum converter placing second, third, and fourth, respectively. The molybdenum converters of Thermo Electron and Rem are easily rejuvenated to 100% using hydrogen for a short period of time.

The detectors and reaction chambers used by the various manufacturers have some very subtle differences--for example, background level variability for ozonator on and off conditions. The Thermo Electron and Rem possess the lowest ozone contribution to background level, while the Bendix has the highest. In addition to background level contributions from ozone, the units were tested using zero air, very dry (dew point -30°F), and slight relative humidity (1-4%). The Bendix unit yielded a greater response for dry air than for air containing a slight amount of moisture.

Light leaks entering the detector cell presented problems in the Thermo Electron analyzer. All analyzers except Thermo Electron utilized stainless steel tubing in the near vicinity of detector parts. Teflon tubing without proper shielding is notorious for conducting light great distances. The Thermo Electron unit utilized two sizes of heat-shrinkable, black tubing, using the larger size over tubing connectors and the smaller size over Teflon tubing to shield it from ambient light. Poor quality control/design allowed it to slip away from the tubing and fittings. This deficiency was relatively easy to correct.

Signal processing can be subdivided into three distinct groups with respect to range circuitry location and type of amplification used and are as follows:

Analyzer	Amplification	Range
Bendix	electrometer (0.5 - 5.0 ppm)	Individual ranges for $NO-NO_2-NO_x$. Range control associated with memory circuits.
Meloy	chopper amplifier demodulator (0.5 - 5.0 ppm)	Individual ranges for $NO-NO_2-NO_x$. Range control associated with memory circuits.
Thermo Electron	range attenuator network input to electrometer (0.5 - 10.0 ppm)	One range for all $NO-NO_2-NO_x$
Rem	range attenuator network input to electrometer (0.5 - 10.0 ppm)	One range for all $NO-NO_2-NO_x$

One significant difference in the analyzers is the feature of individual ranges for $NO-NO_x-NO_2$ under ambient monitoring conditions. NO concentration levels are typically 2 to 5 times higher than NO_2 concentration levels. All analyzers utilize some averaging or integrating step prior to sampling and hold operation of the memories while functioning in the cyclic mode. When operating in the manual mode (i.e., NO or NO_x only), the Bendix and Meloy exhibited a greater noise bandwidth than when operated in the cyclic mode. Lack of adequate radio frequency (RF) shielding and/or design of the ozonator in the Bendix analyzer allowed the RF to propagate into the signal processing electronics and through rectification in the transistor junctions, added and sometimes subtracted values from the actual dc signal level.

Major problems encountered during this evaluation and other field programs with chemiluminescent $NO-NO_x-NO_2$ analyzers involved the gas flow system (i.e., maintaining the required cell pressure), electronic component failures, generation and destruction of high concentrations of ozone, and the cyclic mode of operation where rapid changes in the ratio of NO/NO_2 in ambient air can yield negative NO_2 measurements. These problems were pointed out to the various manufacturers of chemiluminescent $NO-NO_x-NO_2$ analyzers as they occurred, and appropriate recommendations to alleviate the problem were made.

7.3.3 Sulfur Analyzers

Two measurement methods, which utilized the same detection principle, were evaluated. Both a gas chromatographic flame photometric detector (GC-FPD) and a flame photometric detector (FPD) were tested for total sulfur, sulfur dioxide, hydrogen sulfide and total sulfur.

The flow system of GC-FPD analyzers usually consists of sample loop, pump, valves, stripper column, analytical column and detector. Two sample loops may be employed: one for total sulfur and one for the analytical column. The stripper column is used in automated gas chromatographs designed for continuous monitoring. The stripper column removes from the sample aliquot interferences (i.e., H_2O, methyl mercaptans, etc.). After the components of interest elude the stripper column, it is subsequently back-flushed and vents to the atmosphere most of the trapped interferences. For some interferences, the process is nonreversible, giving the column a finite lifetime. The lifetime of the column is dependent on contamination level of the environment sampled, the frequency of analysis, packing material, size of column, and sample size.

The analytical column used in a gas chromatograph will undergo a change in its characteristics with time. Column deterioration is usually recognized by a closing of the space separating the chromatographic peaks, concurrent change in retention times, peak overlap, base broadening, or some combination of these symptoms.

It is imperative to maintain proper operational documentation as follows:

(1) periodically run chromatograms comparing retention times with prior run;
(2) place in record book for future reference;
(3) record data such as flow rate, chart speed, pressure, oven temperature, pollutant concentration, and any additional pertinent parameters; and
(4) record all modifications made by the manufacturer.

The FPD requires proper preventive maintenance for reliable, trouble-free performance. The most important precautions include:

(1) provision for continuous removal of all combustion products including water vapor, and
(2) utilization of sulfur-free carrier gas.

7.3.4 Hydrocarbon Analyzers

The flow system of gc-flame ionization hydrocarbon analyzers usually consists of a pump, sample loop, valves, stripper column, analytical column and detector. Most manuals stress the importance of cleanliness which will be reiterated here. A dirty cylinder outlet, contaminated regulator, or service tubing can foul an analyzer and contribute to poor performance. Each gas cylinder used should be equipped with a clean, hydrocarbon-free, two-stage regulator with appropriate indicating gauges. Each regulator should have a metallic, not elastomeric, diaphragm and have a cleanliness equivalent to materials used in handling liquid oxygen. The use of all new tubing is strongly recommended for all connecting gas lines. The tubing material type should be compatible with the pollutant of interest and the accompanying gases. The material type should not be a source of the contaminant of interest nor an adsorber. Polyethylene tubing is frequently used because of its flexibility, strength, and inertness. In some applications, the preferred type is new "refrigeration grade" copper tubing sealed at the ends. Generally, stainless steel tubing is less desirable, as it contains hydrocarbon contaminants, necessitating scrupulous cleaning before installation. Precleaned "chromatographic grade" stainless steel tubing, available at premium price, is recommended if stainless is to be used. Stainless steel tubing of other than "chromatographic grade" may be used if properly cleaned. The following cleaning procedure is recommended:

(1) Wash with hydrocarbon solvent such as acetone or trichloroethylene.

(2) Rinse with distilled or deionized water.

(3) Connect tubing to the regulator on a cylinder containing nitrogen using a flow rate of 1 to 10 liters per minute.

(4) Heat the tubing with a propane or natural gas torch working the heat source slowly from the regulator end to the open end of the tubing. This will remove contaminants from the inner walls of the tubing and expel them at the open end.

Caution: Never heat lines when connected to a gas chromatograph.

Tubing of questionable cleanliness and new tubing should be cleaned with the exception of "refrigeration" and "chromatographic grade" tubing. It is customary to employ release agents such as oil for metal tubing or talcum for plastic tubing during the manufacturing process.

Tubing such as copper and plastic may be cleaned as follows:

(1) Flush tubing with methylene chloride.

(2) Rinse with acetone.

(3) Purge with an inert gas such as helium or nitrogen.

(4) If cleanliness is questionable, zero-air can be passed through it to the analyzer for a reading and then bypassed. A difference in analyzer reading indicates further cleaning is necessary.

A stripper column is used in automated gas chromatographs designed for continuous monitoring. The stripper column removes from the sample aliquot interferences (i.e., H_2O, CO_2, and hydrocarbons other than CH_4). After the components of interest elude the stripper column, it is subsequently backflushed and vents to the atmosphere most of the trapped interferences. For some interferences, the process is nonreversible, giving the column a finite lifetime. The lifetime of column is dependent on the contamination level of the environment sampled, the frequency of analysis, packing material, size of column and sample size. Failure to replace an expended stripper column will result in the eventual contamination of the analytical column. A degradation of the stripper column and analytical column can yield similar failing symptoms. It is generally recommended to replace the stripper column first if there is doubt about the analytical column. If difficulty is encountered in the analytical column, it is advisable to replace both columns at the same time.

The analytical column used in a gas chromatograph will undergo a change in its characteristics with time. The rate of change may be dramatic, occurring within a few days, or insignificant, over a year's time. Column deterioration is usually recognized by a closing of the space separating the chromatographic peaks, concurrent change in retention times, peak overlap, base broadening, peak flattening and tailing of the top of the chromatogram, or some combination of the symptoms.

It is imperative to maintain proper operational documentation as follows:

(1) periodically run chromatograms comparing retention times with previous run;

(2) place in record book for future reference;

(3) record data such as chart speed, flow rates, pressures, oven temperature, pollutant concentration and any additional pertinent parameters.

The flame ionization detector requires the proper preventive maintenance for reliable trouble-free performance. The most important precautions include:

(1) provide for continuous removal of all combustion products including water vapor;

(2) prevent the contamination of any component with hydrocarbons even in trace amounts;

(3) utilize contaminant-free hydrogen and burner air.

Combustion products or other contaminants allowed to accumulate inside the flame ionization detector form electrical leakage paths between the collector and burner contact. Slight traces of such contaminants can degrade the performance sensitivity of an analyzer almost an order of magnitude. For best performance, it is absolutely necessary that the flame ionization detector be kept free of any kind of contamination.

Proper venting of the flame ionization detector is essential, especially in small trailers or monitoring facilities to prevent pressure disturbances from upsetting the flame. The opening and closing of outside doors in relatively air-tight buildings (1000-4000 ft^3) can produce significant effects in the flame background signal level or can yield false peaks. Detector venting to a protected area outside the building is recommended for two reasons: the internal building static pressure upsets are avoided, and should hydrogen "fail-safe" devices fail, the hydrogen will be safely vented to the outside.

The electronics section in hydrocarbon gas chromatograph analyzers includes the following subsystems: timer, amplifier, peak detectors, memory storage, programming capability, fail-safe circuitry, temperature controllers, automatic baseline zero capability, and power supplies. Timers are generally divided into two categories: (1) line frequency divider circuitry and (2) resistance-capacitance, time-constant-controlled voltage ramp. Both techniques are sufficiently reliable and accurate and easily facilitate programming the various functions to an accuracy of one second.

Automated gas chromatographs usually incorporate electronic zeroing circuits to connect for baseline drift. The programming of the automatic zero is critical and requires periodic checking to ensure it is occurring at the appropriate time. Initiation of the automatic zero too early or too late may result in an inaccurate measurement. Automatic zeroing too early may not have allowed sufficient time for baseline recovery from flow/pressure upsets subsequent to valve switching. Automatic zeroing too late may result in zeroing on the leading edge of peak elution.

The programming of the peak detectors and associated memory circuitry is somewhat less ciritical than automatic zeroing procedures but should receive careful scrutiny.

The analyzer must be correctly calibrated if meaningful data are to be obtained. Errors in labeled concentrations will be directly related to ambient air measurements. Vendors of pressurized calibration mixtures tend to emphasize preparation and certification capability of mixtures far exceeding the specifications of the gas mixture evaluated when received. In approximately a one-year comparison of about twenty cylinders on a relative basis, three major discrepancies occurred: two cylinders contained concentrations that deviated by exactly a factor of 2, and one cylinder mixture contained a diluent of non-air (30% O_2, 70% N_2).

Blended air mixtures that deviate from ambient air (21% O_2, 79% N_2) are unacceptable and will yield incorrect calibration of total hydrocarbon analysis. Oxygen concentration exceeding ambient air causes the analyzer to read a higher total hydrocarbon value than is actually present in the calibration mixture. Verification procedures ultimately rest with the user and are not within the scope of this report.

No major problems were encountered with the operation of the Beckman 6800 after replacement of the analytical column with the updated version prior to the evaluation period. Minor problems were encountered with failure of electronic components and circuitry which required the attention of a component operator. Daily attention by a competent operator is required for optimum performance.

A major problem, requiring an engineering modification, was encountered with the Bendix ambient hydrocarbon analyzer and involved installation of precolumn to remove moisture from the sample prior to injection of the sample directly into the flame for the total hydrocarbon measurement. Abnormally high non-methane hydrocarbon measurements were being obtained and were attributed to moisture by Bendix personnel. Installation of a scrubber column prior to the detection chamber appears to have eliminated the problem. Additional tests are being run to verify that the modification has indeed accomplished its purpose.

7.3.5 Carbon Monoxide Analyzers

Analyzers employing three different measurement principles were evaluated during this study. The measurement principles are infrared fluorescence photodiode detection, non-dispersive infrared capacitance-microphone type detection, and gas chromatograph methanation with flame ionization detection. These principles are described in detail in Section 4.0.

All three measurement principles are tolerant to flow rate changes of ± 20%; however, precautions should be observed to prevent pressurizing the flow system above the normal pressure mode of operation.

The optical-flow systems of the analyzers vary significantly with respect to losses in the transmission optical paths. The Andros infrared fluorescence analyzer can tolerate an approximate 50% decrease in optical transmission efficiency due to condensation, particulates in the sample, infrared source intensity or detector response drift. The signal output is directly related to the ratio of CO^{16} to CO^{18} spectral lines.

The Andros carbon monoxide analyzer has an internal zero air system which was compared periodically with an external zero air source. During the evaluation ambient air containing an average of 1.0 ppm CO was passed through the internal zero module used, and the module produced zero air with 0.05 ppm or less of carbon monoxide. No degradation of the zero module was observed during the evaluation period.

Analyzers employing non-dispersive infrared capacitance-microphone detection schemes are susceptible to condensation of particulates and water vapor. Two sample handling deficiencies were noted for the Bendix analyzer and are as follows:

(1) The input sample filter (8 micron) mounted within the bowl failed to sufficiently remove the water during high humidity periods and allowed condensation in the gas filter mounted within an aluminum housing, external to the analyzer.

(2) Replacement of the gas filter further downstream was difficult and attributed to seizing of the threaded portions of the aluminum housing. This made filter element replacement nearly impossible.

Both problems were reported to Bendix for appropriate modifications.

The flow system for the gas chromatograph was outlined in detail for the total hydrocarbon and methane analysis in the previous section and will not be reiterated here except for pertinent facets of the carbon monoxide measurement. The Beckman 6800 air quality chromatograph utilizes a converter to reduce the carbon monoxide to methane in the presence of hydrogen on a heated nickel catalyst. The conversion efficiency is typically 70 to 100%. Current data indicate a decrease of approximately 5% in one year of operation. Converter efficiency appears to be constant for CO concentrations up to 100 ppm. Converter efficiency was checked by using known concentrations of methane and carbon monoxide and determining the areas under the respective peaks. For equal concentrations it is simply the ratio of the areas. If the converter efficiency is constant between calibration period and not 100%, satisfactory and meaningful data can be obtained by simply increasing the electronic gain of the amplifier. Subsequent CO peak decreases from successive calibrations would warrant checking the converter efficiency. Converter efficiencies appear to be very reliable, and periodic checks are not recommended. With careful maintenance and use of proper calibration and operating procedures, a minimum detectable limit of 0.1 ppm was achieved, using the test procedure specified in Section 5.2.4.

The capacitance-microphone detector utilized in the Bendix analyzer is marginally capable of making CO measurements with a minimum detectable limit in the neighborhood of 1.0 ppm after a few weeks of operation. With careful maintenance, sample conditioning, and use of proper calibration and operating procedures, the minimum detectable limit may be reduced to below 1.0 ppm. This type of detector is very vibration and temperature sensitive, and precautions should be observed for proper location of the analyzer and insulation from vibrations and temperature extremes. Pumps and other monitoring equipment can drastically interfere with optimum performance of the analyzer and should be located accordingly.

The detector employed in the Andros isotope fluorescence analyzer is very rugged and will easily tolerate hostile vibration environments such as helicopters and mobile vans. The solid-state photodiode detector is thermally stabilized at -30°C to achieve maximum sensitivity by a Peltier cooler. With careful maintenance and use of proper calibration and operating procedures, a minimum detectable limit of 0.7 ppm can be achieved, using the test procedures specified in Section 5.2.4.

For convenience in troubleshooting, the Andros 7000 contains a continuous self-check function which will generate a panel-indicated NO-GO if any of the following occur:

(1) Excessive postamplifier signal;

(2) Insufficient postamplifier signal that results in closed loop span's AGC drive voltage being too far negative;

(3) Closed loop span fault, which results in AGC drive voltage being too far positive.

The self-check circuits are all part of the comparator assembly. In addition to generating a panel NO-GO, the comparator has five diagnostic indicators which include a GO as well as a NO-GO situation. There are three other indicators which, if a NO-GO is displayed, indicate which of the above abnormal conditions exist. The indicator lights on the panel and diagnostic lights on the printed circuit board are intended to help identify the probable cause of improper operation, as well as indicate operating modes.

In addition to the above, the automatic frequency control circuit board contains a self-test switch, which sends a control pulse train to the automatic gain control board. This causes an upscale span increment of approximately 50% of full scale. This test procedure will only work if the optical system and the CO^{16} and CO^{18} signals coming from it are in good order.

The GO/NO-GO indicator is the most advanced concept for subsystem component check for air monitoring instrumentation on the market. Each printed circuit board has an individual card guide and retainer. The electronic subsystem is adequately separated and shielded from the pump, plumbing and internal zero. The Andros 7000 evaluated during this study definitely does not have the production line appearance. The development of subsystem component test points and checks is recommended for inclusion on all future analyzers.

7.3.6 General List of Design Deficiencies/Considerations

Results of the subsystem component evaluation indicate certain deficiencies or design considerations that are applicable or common to all instrumentation with respect to the gas flow, detector, and signal processing subsystems. This list of considerations is segmented by subsystem, is presented in outline form, and is by no means all inclusive. The reader is also advised that many of the design considerations presented for one subsystem may also be applicable to other subsystems.

7.3.6.1 Gas Flow Subsystem

(1) Plumbing of sample handling system should be minimized in length and diameter to enhance instrument response time and reduce possible sample deterioration.

(2) Tubing, valves, and filters should be compatible with the pollutant being sampled and measured.

(3) Tubing should have sufficient wall thickness to prevent collapse or pinch-off at tubing bends in the instruments. Operating temperature and the gas being handled should be considered in selecting tubing used in the analyzer.

(4) Hot and cold regions should be avoided in the sample handling system.

(5) Sample handling scrubbers or conditioners that require constant or frequent attention should be avoided. If preconditioning is essential for proper operation, the conditioning element should have a visible or useful life status indicator.

(6) Sufficient monitoring gauges or indicators should be used to warn the user of degradation of performance or upcoming failure of vacuum pumps or other sample handling devices.

(7) Cooling air for components internal to the instrument should be filtered to prevent accumulation or buildup of dirt and dust on electronic component parts.

(8) Avoid using incompatible materials where vibration, temperature, voltage, stress levels, etc., would induce failure (i.e., stainless steel housing for glass capillary where vibration causes glass to fracture).

(9) Particulate filters, preferably Teflon filter elements, should be included on all instrument inlet lines, regardless of the pollutant being measured.

(10) Safety devices, such as automatic shut-off valves which close upon loss of vacuum or AC-line voltage to the instrument should be included for handling hydrogen, oxygen, ethylene, etc.

7.3.6.2 Detector Subsystem

Detectors employing photomultiplier tubes as sensors should be designed with provisions to:

(1) Check the HV with at least one accessible test point.

(2) Check the dark current by use of a shutter in front of the sensor or a positive method for reducing

luminescence to an insignificant amount; the latter might be accomplished by passing a quenching gas into the detection chamber.

(3) Check the gain of the detector assembly by means of a built-in calibrated light source.

A desirable way to check the operation of a detector utilizing a photomultiplier (PM) tube or other type of photo-sensor would involve the use of a calibrated (or known) intensity light source with an output in or near the wavelength(s) of interest. If it is located in the detection cell, then the performance of the entire electro-optical system may be checked out. This would indicate (indirectly) problems with buildup on the detection window, i.e., light transmission, and in the performance of the PM tube. Assuming no change in the light transmission through the detection window, the gain and signal-to-noise (S/N) ratio of the PM tube may be ascertained.

The dark current is a direct function of temperature and any ambient light. A means for recording dark current, under normal operating conditions, is essential to the determination of malfunction in the PM tube, a light leak in the detection, or some unwanted chemiluminescence reaction or prior exposure to light. For example, exposure to ambient light (without voltage applied) may require up to 48 hours before the dark current has returned to its normal and stable level.

The implications of such testing procedures cannot be overemphasized, provided standard techniques are used and the data are recorded for future reference. Such data will be invaluable in the troubleshooting of individual instruments and collecting data which will help indicate trends or degradation rates of the instruments. Compilation of data from several instruments over time will produce the data necessary to statistically describe the distribution of the various performance parameters and allow, to some degree, prediction of individual unit performance as well as indicated individual component weakness or out-of-tolerance situations.

7.3.6.3 Signal Processing Subsystem

(1) Card guides and retainers should be used for all printed circuit cards.

(2) Circuit board contacts should be compatible with connectors. Mechanical vibration of tinned contacts on printed circuit boards mated with gold-plated connectors often yield undesirable resistance, especially in series with control potentiometers.

(3) Electronic subsystems should be adequately isolated or shielded from devices such as valves, ozonators, ovens, and other mechanical subsystems which may induce undue stress from electromagnetic, vibrational, or thermal sources.

(4) Heavy components should not be mounted on printed circuit cards causing undue torque or bending moments.

(5) GO/NO-GO indicators are essential for subsystem checkout and failure isolation. Future development of instrumentation should demand incorporation of these indicators for all feasible subsystem checkpoints.

(6) Instrument controls, such as potentiometers, should be turn-counting with locking-type dials.

(7) Commercially available packaged operational amplifiers and signal processing devices with demonstrated reliability are preferable to home-built devices.

8.0 RECOMMENDATIONS FOR SELECTION OF INSTRUMENTS

Operational requirements, definitions describing sensor specifications, sensor specifications applicable to the special needs of the RAPS Program, criteria for selection of instrumentation, and the test plan were presented in Section 3.0 of this report. Standardized performance evaluation tests were developed to evaluate selected instrumentation on an equivalent basis (Section 5.0). Results of the performance evaluation tests are presented in Section 7.0 along with pertinent comments, observations, and recommendations concerning general deficiencies or considerations observed in the design of selected instrumentation.

Results obtained from the performance evaluation tests were compared to the required specifications and are presented in Table 8.1 for each analyzer. Qualifications that should be considered prior to the interpretation of these results are as follows:

(1) Evaluation results reflect the performance of a single brand-name analyzer assumed to be representative of that brand name; evaluation of a statistically significant number of brand-name analyzers was not possible;

(2) performance evaluation tests were designed and implemented in a uniform manner whenever possible, so that no one analyzer was discriminated against;

(3) test results presented are representative of the performance of each analyzer during its best period of performance (i.e., tests were sometimes interrupted due to failures, modifications, etc., and required rerunning);

(4) test results were invalidated for any analyzer during periods when the analyzer's performance was questionable;

(5) test results are dependent to a large extent on the precision and accuracy of the calibration systems to deliver or generate test atmospheres reliably over long periods of time;

Table 8.1: COMPARISON OF TEST RESULTS TO REQUIRED SPECIFICATIONS

INSTRUMENT		MINIMUM DETECTABLE CONCENTRATION (PPM)			PRECISION (%)		DRIFT/WEEK (%)						LINEARITY (PPM)		OPERATIONAL PERIOD (DAYS)	
		RAPS SPEC.	EVALUATION TEST RESULT (90%)	EVALUATION TEST RESULT (60%)	RAPS SPEC.	EVALUATION[1] TEST RESULT	RAPS SPEC. ZERO	EVALUATION TEST RESULT S.D.	EVALUATION TEST RESULT $\bar{X}$	RAPS SPEC. SPAN	EVALUATION TEST RESULT S.D.	EVALUATION TEST RESULT $\bar{X}$	SUGGESTED[2] S.D.	EVALUATION TEST RESULT S.D.	RAPS SPEC.	SUGGESTED PERIOD
BENDIX 8002	O_3	0.005	0.005	0.003	2.0	4.5	5.0	0.1	0.03	4.0	3.0	-0.50	0.002	0.0005	14	7
DASIBI 1003-AH	O_3	0.005	0.008	0.004	2.0	6.0	5.0	*	*	4.0	*	*	0.002	0.0007	14	7
BENDIX 8101-B	NO	0.005	0.031	0.016	2.0	1.8	3.0	0.4	-0.05	2.0	1.1	-0.68	0.004	0.0090	14	7
BENDIX 8101-B	NO_2	0.005	0.005	0.003	2.0	1.3	3.0	0.4	-0.16	2.0	0.9	-0.62	0.002	0.0010	14	7
MELOY 520	NO	0.005	0.070	0.034	2.0	4.1	3.0	1.5	0.68	2.0	6.9	2.80	0.004	0.0270	14	3
MELOY 520	NO_2	0.005	0.025	0.012	2.0	4.4	3.0	.5	0.21	2.0	6.4	3.35	0.002	0.0060	14	3
REM 642	NO	0.005	0.118	0.059	2.0	9.0	3.0	**	**	2.0	**	**	0.004	0.0280	14	3
REM 642	NO_2	0.005	0.027	0.013	2.0	2.4	3.0	**	**	2.0	**	**	0.002	0.0110	14	3
THERMO ELECTRON 14	NO	0.005	0.016	0.008	2.0	1.7	3.0	0.3	-0.01	2.0	2.2	0.00	0.004	0.0039	14	10
THERMO ELECTRON 14	NO_2	0.005	0.009	0.0005	2.0	3.4	3.0	0.2	0.06	2.0	2.5	-0.80	0.002	0.0033	14	10
BENDIX 8300	TS	0.005	0.008	0.004	2.0	3.3	3.0	5.0	1.82	2.0	10.7	4.18	0.004	0.0043	14	4
MELOY SA-185R	TS	0.005	0.007	0.004	2.0	1.5	3.0	0.8	-0.04	2.0	2.5	-0.38	0.004	0.0036	14	7
TRACOR GC 270-HA	TS	0.005	0.016	0.008	2.0	0.6	3.0	0.3	0.00	2.0	9.2	-2.4	0.004	0.0043	14	3
TRACOR GC 270-HA	SO_2	0.005	0.016	0.008	2.0	0.9	3.0	0.2	-0.05	2.0	8.0	-2.3	0.004	0.0045	14	3
TRACOR GC 270-HA	H_2S	0.002	0.006	0.003	2.0	2.4	3.0	0.2	0.06	2.0	3.1	0.6	0.004	0.0010	14	3

1 - Precision (%) = [3 × Standard Deviation of Precision (Table 7.3)/Measurement Range Setting × 100]
S.D. - Standard Deviation
$\bar{X}$ - Mean
* - Not Available for Complete Test
2 - Recommended (not specified)

Table 8.1: COMPARISON OF TEST RESULTS TO REQUIRED SPECIFICATIONS (Cont'd)

INSTRUMENT		MINIMUM DETECTABLE CONCENTRATION (PPM)			PRECISION (%)		DRIFT/WEEK (%)						LINEARITY (PPM)		OPERATIONAL PERIOD (DAYS)	
			EVALUATION TEST RESULT					EVALUATION TEST RESULT			EVALUATION TEST RESULT					
		RAPS SPEC.	(90%)	(60%)	RAPS SPEC.	EVALUATION[1] TEST RESULT	RAPS SPEC. ZERO	S.D.	$\bar{X}$	RAPS SPEC. SPAN	S.D.	$\bar{X}$	SUGGESTED[2] S.D.	EVALUATION TEST RESULT S.D.	RAPS SPEC.	SUGGESTED PERIOD
ANDROS 7000	CO	0.100	0.74	0.37	1.0	0.7	3.0	0.1	-0.16	2.0	1.4	-0.56	0.100	0.3200	30	10
BENDIX 8501-5FA	CO	0.100	0.82	0.41	1.0	3.0	3.0	0.4	1.56	2.0	1.0	0.14	0.100	0.0160	30	3
BECKMAN GC 6800	CO	0.100	0.12	0.06	1.0	2.0	3.0	1.8	-0.42	2.0	3.1	0.78	0.100	0.3290	30	3
BECKMAN GC 6800	THC	0.100	0.05	0.03	1.0	0.4	3.0	1.9	0.14	2.0	1.6	-0.24	0.050	0.0180	30	3
BENDIX GC 8201	THC	0.100	0.08	0.04	1.0	1.0	3.0	0.9	-0.27	2.0	2.4	1.27	0.050	0.0210	30	3
BECKMAN GC 6800	CH_4	0.100	0.04	0.02	1.0	0.3	3.0	0.3	-0.04	2.0	1.9	0.96	0.050	0.0058	30	3
BENDIX GC 8201	CH_4	0.100	0.14	0.07	1.0	1.1	3.0	0.7	-0.35	2.0	1.7	0.88	0.050	0.0162	30	3

1 - Precision (%) = [3 × Standard Deviation of Precision (Table 7.3)/Measurement Range Setting × 100]
S.D. - Standard Deviation
$\bar{X}$ - Mean
* - Not Available for Complete Test
2 - Recommended (not specified)

(6) resolution of data down to ppb levels is possible only by digital data resolution and computer processing of data; and

(7) test results depend to a large extent upon the design of the experiment or test used to determine the instrument performance specification; all data presented in Table 8.1 were obtained using the performance evaluation tests described in Section 5.0.

Important observations that should be noted from Table 8.1 and discussed are as follows:

(1) A significant number of analyzers failed to meet the performance criteria for minimum detectable concentration. The minimum detectable concentration was determined using a confidence level of 90%; however, if the confidence level were reduced to approximately 60%, more than half of the analyzers would meet the performance specification. In addition to the above, an improvement in calibration systems, especially the hydrocarbon and carbon monoxide standards, would significantly improve the lower detection limits.

(2) Most analyzers easily met the zero drift specification, with only two analyzers demonstrating appreciable monotonic drift. This can be observed by comparing the mean value and the standard deviation. The larger the mean value, the greater the departure from random drift.

(3) The number of analyzers meeting the span drift performance standard were almost equally divided. Recent modifications and incomplete test data on the Bendix sulfur analyzer indicate a substantial improvement in its span drift characteristics. The Tracor GC 270-HA analytical column and detection systems are potentially capable of better performance than demonstrated during this evaluation.

With improved design and upgrading of the electronic subsystems, span drift should be capable of being reduced to acceptable levels.

(4) Over one-half of the analyzers exceeded the linearity performance criteria. Several analyzers failed by very small margins approaching the testing capability. Retesting and/or very minor modifications would make most analyzers meet linearity performance parameters.

(5) Signal output noise from the analyzers was not compared since almost all exceeded the specifications for a monitoring system.

(6) None of the instruments evaluated could meet the specification of 14 to 30 days' unattended operation; however, a 7- to 15-day period of unattended operation may be achieved.

Recommendations for selection of instrumentation for the RAPS Program that can meet most of its requirements can better be accomplished by verifying that instrumentation based on the specified measurement principle exists, than by naming specific brands for purchase. Recommendation of specific instruments would be hazardous, in that all available analyzers for each category could not be included in the evaluation and improved and updated versions of specific analyzers are occurring every day. For instance, design changes suggested to several manufacturers months ago are presently being incorporated into the design of the particular analyzer and should contribute to improved performance for future models.

Close examination of the performance evaluation results indicates none of the analyzers evaluated met all the required specifications, some came close to meeting most of the specifications, and others failed to meet many, if not all, of the specifications. In most cases where a particular analyzer failed to meet the required specification, poor performance could usually be attributed to minor deficiencies, such as poor quality control, use of underdesigned components, cheap components to save on initial costs, and poor design, rather than major flaws in the measurement principle. These shortcomings can be overcome when users of equipment at the local/State/Federal level demand that manufacturers be required to demonstrate that their equipment meets minimum performance specifications as measured by a uniform, standardized testing procedure. Until such a program is implemented, equipment manufacturers will continue to market air quality instrumentation which is underdesigned for manufacturing cost-savings, has not been properly evaluated for field monitoring prior to release, and is continually updated and/or redesigned as users discover deficiencies through field use and/or instrument evaluation programs.

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APPENDIX A RECOMMENDED CALIBRATION PROCEDURES

Recommended calibration techniques and detailed calibration procedures utilized for this evaluation program to provide standard calibration concentrations were presented in Section 6.0 of this report. The purpose of this section is not simply to reiterate what was presented in Section 6.0, but to expand on the subject area and discuss the philosophy and recommend frequency of calibration, advantages, disadvantages, reliability, precision and accuracy of current calibration systems, problems encountered in calibration of particular instruments, reliability and accuracy of commercially available calibration gases (i.e., cylinders), and quality control procedures applicable to calibration and operation of continuous analyzers.

Dynamic calibration procedures are recommended for calibration of all continuous air quality analyzers. Static methods were useful at one time for performing detector system checks, but serve no useful purpose for calibration of present day state-of-the-art instrumentation. This does not mean, however, that the development of specific test point checks should not be pursued for verification of subsystem component performance (i.e., test points to verify proper operation of electrometer amplifiers, power supply systems, photomultiplier tubes, flow rates, etc.). Properly designed test indicators could be invaluable aids for maintenance, operational, and troubleshooting of ambient air analyzers.

Recommended calibration techniques, optimum frequency of calibration, and precision and estimated accuracy of the calibration procedure are presented for each set of analyzers (i.e., O_3, NO_x, SO_2, HC, CO) in Table A-1. The optimum frequency recommended for calibration of continuous air quality analyzers consists of daily zero and span checks with multipoint (zero plus four calibration points) calibration at biweekly intervals. This frequency of calibration has been found to be sufficient to insure reliability of data and characterize instrument performance. It is readily apparent that the proper use of calibration procedures and optimum calibration schedules are paramount in assuring the collection of quality data.

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Table A-1. RECOMMENDED CALIBRATION PROCEDURES

Pollutant	Calibration Method	Calibration Frequency*	Precision of Calibration	Estimated Accuracy of Method
Ozone	UV-ozone generator referenced to KI Method (Federal Register)	Zero, span daily; multipoint biweekly	± 2%	± 5%
Sulfur Dioxide	NBS Permeation Tube	Zero, span daily; multipoint biweekly	± 2%	± 2%
Nitric Oxide/ Nitrogen Dioxide	Gas Phase Titration (Federal Reference Method)	Zero, span daily; multipoint biweekly	± 2%	± 5%
Hydrocarbons**	Cylinder gas (CH_4 in HC-free air)	Zero, span daily; multipoint biweekly	± 2%	± 2%
Carbon Monoxide**	Cylinder gas (CO in air)	Zero, span daily; multipoint biweekly	± 2%	± 2%

* Optimum calibration frequency.

** Manufacturer's stated concentration should be verified.

During the evaluation program, problems were encountered in the calibration of certain analyzers utilizing the techniques described in Section 6.0 and summarized in Table A-1. These problems along with pertinent comments and observations are presented for each calibration procedure (i.e., O_3, NO/NO_2, SO, HC, CO) in the following paragraphs.

No problems were encountered with calibration of ozone instrumentation using the UV-ozone generator, which was referenced to the Federal Reference Method (Neutral-Buffered KI Procedure). It is readily apparent, however, to experienced personnel that the precision of generation of ozone concentration by the UV-ozone generator, once calibrated, is far superior to the precision and accuracy achievable with the manual Neutral-Buffered KI Procedure for verification of the ozone concentrations. It has also been demonstrated that once calibrated, the UV-ozone generator described in Section 6.1 can be used reliably in the field for calibration purposes for several months without further verification. Calibration concentrations generated by this technique should be referenced to and verified by the manual Neutral-Buffered KI Procedure at least once every two months over the ozone measurement range normally encountered at the particular monitoring site (i.e., full scale range setting of measuring instrument). Although the precision of generation of ozone by this technique has been shown to be better than ± 2%, the accuracy of ozone measurement can be no better than the accuracy of the reference method in the absence of a primary standard for ozone. Therefore, the accuracy of the ozone measurement should not be reported as being better than ± 5%. In the absence of a primary ozone standard, absolute measurements of ozone concentration in ambient air are not achievable at this time.

No problems were encountered in calibration of total sulfur analyzers with calibration concentrations generated by SO_2 permeation tubes. Certified SO_2 permeation tubes can be obtained from the National Bureau of Standards as a primary standard for SO_2. The major problem is maintaining the permeation tube at a constant temperature of ± 0.1°C. Calibration apparatus are available commercially that utilize constant temperature water or thermoelectric-cooled permeation tube holders. The main precaution when using permeation apparatus that employs extremely low flow rates, Teflon tube holders, and low-output permeation tubes is to always maintain a sufficient flow rate over the permeation tube to prevent buildup of SO_2 in the permeation tube holder and entrapment of SO_2 in the flow-dilution system. The precision and accuracy of this calibration procedure are quite adequate to insure quality acquisition of SO_2 ambient air data.

Calibration of chemiluminescent NO-NO_x-NO_2 analyzers with the gas-phase titration of NO with ozone was recommended due to problems encountered with field use of NO_2 permeation tubes. As yet, the National Bureau of Standards has not been willing to certify NO_2 permeation tubes as a primary standard for generating NO_2 test atmospheres. The gas-phase titration technique has been shown to be an acceptable, precise, and accurate way to calibrate chemiluminescent NO-NO_x-NO_2 analyzers. The primary consideration is, again, the accuracy of the reference method for the iodometric calibration of the UV-ozone generator incorporated into the calibration apparatus. Accuracy better than ± 5% is not achievable under these circumstances, although the precision of generation of NO and NO_2 calibration concentration is on the order of ± 2%. This technique offers the advantage of being able both to generate NO and NO_2 calibration and to allow the operator to determine the conversion efficiency of the catalytic converter (reduces NO_2 to NO), whenever desired. The converter efficiency should be verified during each calibration, both daily zero and span calibrations and multipoint calibrations at two-week intervals. The accuracy and reliability of NO_2 data obtained by the chemiluminescent technique are highly dependent on maintaining a constant converter efficiency, preferably as close to 100% as possible. Verification of the NO in N_2 cylinder concentration should be performed at two-month intervals. Precautions should also be taken to verify the calibration of the UV-ozone generator at two-month intervals.

One problem was encountered with the gas phase titration system and involved using compressed, dry air filtered through charcoal for zeroing the Bendix NO-NO_x-NO_2 analyzer. An erroneous high zero was obtained, which could be attributed to the absence of moisture in the zero air stream.

The discrepancy between zero obtained from dry air versus air containing some moisture as is encountered when using the Bendix zero air module or when monitoring ambient air, was on the order of 2%. Negative numbers often result when erroneous zeroes are obtained and ambient levels of NO and NO_2 are near zero. Design changes in the flow system have been suggested to Bendix to eliminate this problem. No other chemiluminescent NO-NO_x-NO_2 analyzers evaluated exhibited this effect.

Calibration of hydrocarbon and CO analyzers using cylinder of compressed gas mixtures is the ideal method, in that the source of gas is readily accessible, can be used by unskilled personnel, requires no elaborate accessory equipment, produces the stated calibration concentration on demand, and is inexpensive when compared to other calibration systems (i.e., permeation tube calibration systems, gas phase titration, etc.). Major disadvantages using cylinders in calibration of hydrocarbon or carbon monoxide analyzers are: (1) size and weight of cylinders; (2) unavailability of reference standards for comparison with manufacturer's certification of component content; (3) stability factors for component, especially at low concentrations (i.e., carbon monoxide in air); and (4) lack of quality control among suppliers of blended calibration mixtures. Several mixtures of CH_4 and CO in hydrocarbon-free air and zero air obtained from various manufacturers of speciality gases were utilized in this program to determine performance specifications for analyzers having the capability to measure non-methane hydrocarbons and carbon monoxide. As a result of this effort, several observations became readily apparent;

(1) Zero air certified to contain less than 0.1 ppm (65.4 $\mu g/m^3$) hydrocarbons as CH_4 was not acceptable for zeroing hydrocarbon analyzers trying to discriminate non-methane hydrocarbons in the range 0-0.240 ppm (0-157 $\mu g/m^3$);

(2) The manufacturer's certification of analysis cannot be accepted without further reference to some other standard (i.e., several cylinders were received with the wrong analysis);

(3) Inaccuracies and unreliability of standard calibration gases biased the evaluation results for each analyzer unfavorably;

(4) Calibration of non-methane hydrocarbon analyzers with CH_4 is not totally adequate, but unfortunately, no one can at present specify the composition of non-methane hydrocarbons in ambient air;

(5) Future procurement of CH_4 in hydrocarbon-free air should specify an analysis for CH_4 and total hydrocarbons as CH_4; these two analyses are usually not the same and cause extreme difficulties when calibrating instruments having the capability to discriminate non-methane hydrocarbons;

(6) Cylinder gas containing CH_4 in air is stable for at least six months at concentrations greater than 1.0 ppm; cylinder gas containing CO in air at low ppm levels is not as stable and its concentration should be verified at monthly intervals;

(7) Blended air is not acceptable for producing CH_4 and CO standard calibration concentrations, unless the oxygen concentration can be maintained to that normally encountered in ambient air (i.e., 21.0 ± 0.5%). Oxygen enriched moisture of CH_4 in air produce elevated response for total hydrocarbon measurements as methane.

(8) Quality control procedures should be upgraded within the speciality gas industry; and

(9) Primary reference standards for hydrocarbon and carbon monoxide should be developed and marketed by the National Bureau of Standards.

The accuracy, and hence the usefulness, of data obtained from air monitoring instrumentation and surveillance programs are dependent to a great extent upon the ability to calibrate the instrument under actual operating conditions. This can only be accomplished by the acceptance and proper use of standardized calibration techniques and procedures and requires implementation of quality assurance programs at state, regional, and the federal levels to insure the orderly development of more precise and accurate methods for calibration and also requires some mechanism to insure the interrelatibility between data being generated by various organizations. Otherwise, a large storehouse of information will become unusable simply because no one can place any confidence in the numbers.

ALTERNATE PROCEDURE FOR GENERATION OF CALIBRATION QUALITY ZERO AIR

Generation of zero air at monitoring sites is an attractive feature that needs to be considered from the standpoint of cost and convenience. As was previously stated, zero air can be commercially obtained in pressurized cylinders and specified to contain less than 0.01 to 0.1 ppm hydrocarbons as methane and 0.1 ppm carbon monoxide. Typical test results conducted on zero grade air obtained from several manufacturers are as follows:

Certified Cylinder	Measured Value
less than 0.01 ppm THC	0.05 ppm
less than 0.1 ppm THC	0.150 ppm
less than 0.1 ppm THC	0.200 ppm

As an alternate means of generating zero air, one air purifier was tested during this evaluation and yielded zero air of higher quality than presently available in compressed gas cylinders. The quality of zero air generated by this system was dependent upon flow rate and contamination levels. To remove the contaminants from air, a catalytic oxidizer was used to convert hydrocarbons and carbon monoxide to carbon dioxide and water. Ozone is also converted to oxygen in the process. The oxidizer employs a temperature-controlled, two-stage oxidation system which reduces hydrocarbons to less than 0.1 ppm (measured as methane) in its primary catalyst bed. A second catalyst bed reduces carbon monoxide to less than 0.1 ppm. The oxidizer was tested using zero air from pressurized cylinders certified to contain less than 0.1 total hydrocarbon as methane and

0.1 ppm carbon monoxide. Using a flow rate of 200 cc/min for producing hydrocarbon-free, zero air and 2.0 ℓ/min for carbon monoxide, the total hydrocarbon concentration was determined to be 0.02 ppm measured as methane and the carbon monoxide concentration was 0.05 ppm. In all cases, zero air of a higher quality was produced by using the catalytic oxidizer system in conjunction with zero air purchased in cylinders.

Frequently, it is desirable to process ambient air to produce zero air for use in calibration of ambient air analyzers. Ambient air usually contains sufficient moisture to cause condensation or act as an interferent in the calibration system used for generating test atmospheres. One method of effectively removing moisture from air is through the use of a heatless dryer. Such a dryer uses two packed columns; while one column is passing dry air to be used, the other column is vented to the atmosphere to allow backflushing to exhaust the unwanted water. Such a drying system is very effective and can be used satisfactorily for supplying dry air; however, the resulting air tends to be oxygen enriched.

Such oxygen enrichment may cause difficulty with ozone, gas-phase titration of NO_2, and hydrocarbon calibrations should the air supply be interchanged with a compressed zero air cylinder. The oxygen enriched air will yield slightly higher ozone and nitrogen dioxide concentrations and give an elevated hydrocarbon response using flame ionization detectors. Air purification systems are commercially available that utilize the heatless dryer in conjunction with a catalytic converter to produce both dry air for calibration purposes (i.e., zero and diluent air for O_3, SO_2, and NO, NO_2 analyzers) and chromatographic-grade air for combustion air for gas chromatographic-flame ionization detector analyses.

APPENDIX B RECOMMENDED OPERATING PROCEDURES

The purpose of this section is not simply to reiterate the instructions supplied by the manufacturer for operating each analyzer, but to discuss the philosophy and recommend, based on experience and experimental evidence, optimum operating procedures for a total air monitoring system. Factors which must be considered are specification of space requirements and operating environment (temperature and humidity controls), power requirements, air sampling and inlet systems, and data acquisition systems. These factors will be considered independent of recommended operating and calibration requirements for each set of analyzers (i.e., O_3, NO_x, SO_2, HC, CO). Recommendation of optimum operating procedures for each set of analyzers can best be accomplished by (1) reiterating those procedures specified by the manufacturer and (2) pointing out any additional procedures that need to be incorporated into the operational procedure to improve performance and prevent excessive downtime. For the sake of brevity, operating procedures recommended by the manufacturer will not be presented; however, the reader is advised to review in detail and follow the operational procedures supplied in the instruction manual accompanying each analyzer. Only those additional procedures that need to be incorporated into the operating instructions will be presented in this section for each set of analyzers.

Space and an optimum operating environment are important considerations for any monitoring system. Proper selection of shelter design and size is required to provide the necessary housing for analyzers, data recording and calibration systems, and personnel. Space requirements will vary with the sophistication of the station in terms of monitoring requirements and data acquisition capabilities. To adequately house instrumentation for the measurement of O_3, $NO-NO_x-NO_2$, SO_2, $THC-CH_4-NMHC$, and CO in ambient air, accessory equipment, data acquisition and calibration systems, and associated test equipment, a shelter with a minimum of 250 sq. ft. is recommended. Consideration should also be given to maintaining the aesthetic quality of the surrounding environment or neighborhood and should dictate the exterior design of the shelter.

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Control of temperature and humidity to close tolerances is required for optimum operation of air quality analyzers, regardless of the manufacturer or model. Requirements will vary from analyzer to analyzer depending on the principle of operation and other design factors. Therefore, temperature and humidity specifications should be designed around the analyzer or analyzers most affected by or subject to variation in environmental extremes. The following temperature and humidity ranges are recommended for optimum operation of air monitoring systems, air quality analyzers, and automatic data acquisition systems with telemetry and computer processing capabilities:

(1) ambient temperature - 72° ± 3°F

(2) humidity - - - - - - - 30 - 50% R.H.

Design of air conditioning/heating systems should anticipate heat load requirements, provide good distribution of heat/cooling air flow to minimize temperature extremes (i.e., hot/cold spots), and be capable of maintaining the required temperature and humidity specifications within the stated tolerances over an exterior ambient temperature range consistent with that typically experienced in the area where the site is to be located.

Regulation of AC-line voltage is recommended for optimum operation of all analyzers, regardless of manufacturer or model, stripchart recorders, and automatic data acquisition systems with computer processing capabilities. Regulators are available which are capable of maintaining AC-line voltage to 117 volts ± 2 volts, while supplying 30 to 40 amps of power. This is sufficient to satisfy the regulated power requirements for the entire air monitoring system. Regulation of line voltage variation removes one more variable that can affect proper operation of instrumentation under adverse conditions of extremes in line voltage.

Air sampling, inlet manifold, inlet sampling lines, and all surfaces with which the air sample comes into contact should be selected to maintain the integrity of the sample and minimize losses due to wall absorption and reaction with surfaces. To maintain the integrity of the air sample, inlet manifold and air sampling systems constructed of Teflon and glass are recommended throughout. Instrument inlet sampling lines should be constructed of Teflon and be as short as possible. As was stated in Section 2.2, laminar flow is not required in the manifold to prevent losses of pollutants due to wall adsorption or reaction. An air sampling system consisting of 1- to 2-in (2.54-5.08 cm) O.D. glass tubing with bushings and Viton O-ring connectors and a flow rate of 50 to 100 liters per minute through the manifold is sufficient for any air monitoring system. Larger glass manifold tubing may be used but requires higher investment costs. Location of the manifold inlet should be at least 1 meter above the roof surface, and a flower pot or cane arrangement should be used to prevent moisture and large particulates from settling into the manifold. It is also advisable to include a particulate and condensation collection bottle at the base of the inlet line. All glass inlet lines should be thoroughly cleansed prior to use and cleaned periodically, as needed. For instance, experience has shown that some conditioning of the surfaces of the manifold inlet line is required with ambient air after cleansing to prevent initial loss of ozone.

Additional procedures recommended for incorporation into the operating instructions supplied by the manufacturers for each set of analyzers (i.e., O_3, NO_x, SO_2, HC, CO) or procedures that need to be reiterated are presented in outline form in the following paragraphs. These recommendations cover many aspects that can be related to safety, to optimum operation of the facility as well as the analyzer itself, and to general rules of good practice for operation of an air monitoring system. Recommended procedures applicable to the operation of instrumentation based on different measurement principles are presented together, in cases where analyzers with different measurement principles were evaluated in this study. Thus, some recommendations may not apply to both measurement techniques if two were evaluated. As stated before, the reader should refer to and follow all instructions specified in the instruction manual supplied with the respective analyzer.

A. OZONE INSTRUMENTATION (Chemiluminescent Principle)

(1) Precautions should be taken to ensure a leakless system for the ethylene supply. In addition, a catalytic oxidation unit or some other device should be incorporated to oxidize or destroy ethylene in the exhaust stream from the analyzer. The exhaust line should be vented to the outside exterior of the shelter. Destruction of the ethylene is warranted from a safety standpoint and to prevent contamination of the air sampling system with the ethylene, a non-methane hydrocarbon. Precautions should be taken to safely dispose of or destroy percentage quantities of ethylene.

(2) Never operate an ozone analyzer without a particulate filter on the sample inlet line. Construction of the filter and filter element should be of Teflon. Change the filter element as required.

(3) Teflon or glass tubing are the only materials recommended for use for the sample inlet line. Teflon tubing is preferred.

B. OXIDES OF NITROGEN (Chemiluminescent)

(1) Precaution should be taken to ensure a leakless system if oxygen is used for the ozonator supply. Ozone must be destroyed prior to venting to the atmosphere. Ensure that the destructive agent (charcoal, thermal decomposition, etc.) is replaced as required. Vent the exhaust line to the outside exterior of the shelter.

(2) Include provisions for monitoring cell pressure in the daily operational procedures. Replace vacuum pump if cell pressure decreases by 2.54 cm of Hg or recalibrate analyzer, whichever is more practical. Regardless, replace vacuum pump when it can no longer maintain the required cell pressure specified by the manufacturer.

(3) Never operate NO_x analyzers without a particulate filter on the sample inlet line. Construction of the filter holder and filter element should be of Teflon. Change the filter element as required.

(4) Teflon or glass tubing are the only materials recommended for use as the sample inlet line. Teflon tubing is preferred.

C. SULFUR DIOXIDE (Flame Photometry)

(1) Precautions should be taken to ensure a leakless system for the hydrogen supply and plumbing system. Vent exhaust from analyzer to the outside exterior of the shelter.

(2) Use of a particulate filter on the sample inlet line to remove particulates is recommended, preferably one constructed of Teflon with a Teflon filter element.

(3) Incorporate a heated silver gauze or wire filter into the sample inlet system to remove hydrogen sulfide and mercaptans if SO_2 data are desired. Otherwise, report the data as total sulfur, measured as SO_2.

(4) Teflon or glass tubing is the only material recommended for use as the sample inlet line. Teflon tubing is preferred.

D. TOTAL SULFUR, SULFUR DIOXIDE, HYDROGEN SULFIDE
(GC-Flame Photometry)

(1) Precaution should be taken to maintain integrity of the hydrogen supply and plumbing system. Vent the exhaust from the analyzer to the outside exterior of the shelter.

(2) Use of a Teflon filter holder and filter element is recommended on the sample inlet line to remove particulates.

(3) Teflon or glass tubing is the only material recommended for use as the sample inlet. Teflon tubing is preferred.

E. TOTAL HYDROCARBONS, METHANE, CARBON MONOXIDE
(GC-Flame Ionization)

(1) Precautions should be taken to maintain the integrity of the hydrocarbon supply and the plumbing system. Vent the

exhaust from the analyzer to the outside exterior of the shelter. This is important, since sudden pressure changes in the shelter interior caused by opening and closing the door will affect the flame.

(2) Never operate a GC-analyzer on ambient air without a particulate inlet filter. Glass fiber or membrane filter elements are satisfactory, provided the pressure drop across the filter element does not restrict air flow.

(3) Use dryers on all gas supplies (hydrogen, burner air, etc.) as specified by the manufacturer.

(4) Use of two-stage, metal-diaphragm regulators is recommended for all compressed gas cylinders (i.e., hydrogen, air, calibration gases).

(5) Use of Teflon tubing for sample inlet lines is not recommended, due to outgasing of the Teflon and permeation of hydrocarbons through the Teflon walls. Use of chromatographic grade stainless steel tubing is recommended.

F. CARBON MONOXIDE (GC-Flame Ionization, NDIR, D.I. Fluorescence - IR Detection)

(1) Precautions listed in Part E apply equally to measurement of CO by GC-flame donization detection.

(2) Use of particulate filters on sample inlet lines is recommended. Glass fiber or paper filters are satisfactory.

(3) Teflon, glass, stainless steel, copper, or polyethylene tubing is satisfactory material for use as sample inlet lines.

The above mentioned precautions and procedures are recommended for optimum operation of air quality analyzers in conjunction with those specified by the respective manufacturers but are by no means all inclusive.

Data acquisition capabilities and facilities will vary with the sophistication of the air monitoring system and the monitoring requirements for which the system was designed. This capability can range from a mere stripchart recorder for a single analyzer to an on-line computer with telemetering capabilities for a full complement of analyzers. Best practice dictates the use of stripchart recorders for all instrument outputs, even though automatic data acquisition systems with computer processing capabilities are available. The stripchart recording provides a visual record of the instrument's performance over the past 24 hours, serves as a backup for retrieval of data when failures occur in the automatic data acquisition system or computer, and is an invaluable aid during instrument calibration and checkout.

APPENDIX C

RECOMMENDED MAINTENANCE PROCEDURES

APPENDIX C RECOMMENDED MAINTENANCE PROCEDURES

Recommendation of maintenance procedures for each analyzer can best be accomplished by (1) reiterating those specified by the manufacturer and (2) pointing out any additional procedures that need to be incorporated into the maintenance schedule to improve performance and prevent excessive downtime. In most cases the procedures recommended by the manufacturer will suffice. For the sake of brevity, recommended maintenance procedures are presented in outline form for each analyzer. It should be noted that these procedures are recommended based on the particular instrument design as it existed in early Spring 1973. Accordingly, the reader is advised to review in detail and follow the maintenance procedures supplied in the instruction manual accompanying each analyzer.

1. BENDIX MODEL 8002 CHEMILUMINESCENT OZONE METER

(a) Replace Teflon element of the sample air filter as required by particulate loading in the area of the monitoring site (at least once/two weeks).

(b) Replace calibration sample filter chemicals (mole sieve, silica gel, charcoal) as needed (at least once/three months).

(c) Replace stainless steel mesh element of ethylene filter as needed.

(d) Replace ethylene cylinder when cylinder pressures decreases to 100 psig.

(e) Examine reed valves of evacuation pump and perform maintenance as specified in instrument manual if pump performance degrades to the point where it will not maintain the proper sample plus ethylene flow rate.

(f) Refer to "Troubleshooting Section" of the instruction manual to isolate problems and determine the cause of failure.

2. DASIBI MODEL 1003-AH UV-ABSORPTION OZONE ANALYZER

(a) Visually inspect interior and exterior instrument and remove excessive dust accumulation.

(b) Clean the absorption chamber and the absorption chamber windows and mirrors at least once/six months.

(c) Replace the ozone catalyst as required (at least once/six months).

(d) Replace the particulate or aerosol filter as required (at least once/month).

(e) Refer to the "Troubleshooting Section" of the instruction manual to isolate problems and determine the cause of failures.

3. BENDIX MODEL 8101-B CHEMILUMINESCENT NO-NO_x-NO_2 ANALYZER

(a) Replace Teflon element of the sample air filter as required (at least once/month).

(b) Replace charcoal in the exhaust filter on a monthly basis.

(c) Replace oxygen cylinder when pressure decreases to 100 psig and the stainless steel mesh element of the oxygen filter as needed.

(d) Observe cell pressure on a daily basis by noting the vacuum gauge reading. Replace pump if pump performance degrades to a point that it will not maintain at least 23 inches of Hg (58.42 cm) vacuum. Changes in cell pressure of 1 inch of Hg (2.54 cm) require recalibration of the analyzer.

(e) Clean instrument interior of accumulated dust by using low velocity air from a compressed cylinder.

(f) Clean the residue buildup off the ozonator electrode on a monthly basis.

(g) Monitor the sample air inlet and vacuum pump outlet flow rates on a weekly basis to insure proper gas flows.

(h) Refer to the "Troubleshooting Section" of the instrument manual to isolate problems and determine causes of failures.

4. MELOY MODEL 520 CHEMILUMINESCENT NO-NO_x-NO_2 ANALYZER

(a) Replace particulate filters as required. Manufacturer recommendes once/year; however, this may not be adequate for all environments.

(b) Replace flow controller assembly as required. Manufacturer recommends once/two years.

(c) Replace zero and span valves every 36 months and the sample switching valve every 24 months or upon failure.

(d) Replace charcoal in de-ozonizer filter on a monthly basis.

(e) Replace vacuum regulator every 12 months and the vacuum pump every 24 months or upon failure.

(f) Replace catalytic converter as required (at least once/year). Converter is rated at 1000 ppm-hrs of NO_2.

(g) Replace or clean window/filter arrangement of detector as required (at least once/year) and/or other components of the detector/chopper unit as needed.

(h) Refer to the "Troubleshooting Section" of the instruction manual to isolate problems and determine the cause of failures.

5. THERMO ELECTRON MODEL 14 CHEMILUMINESCENT NO-NO_x-NO_2 ANALYZER

(a) Replace Balstron filter as required (at least once/year). Replacement is signaled when white portion of the filter is black.

(b) Replace or recharge desiccant in air dryer for ozone generator as required.

(c) Recharge the activated charcoal de-ozonizer filter at 12-month intervals, or more frequently if needed.

(d) Check the converter efficiency at five points in the measurement range on at least a monthly basis.

(e) Refer to the "Troubleshooting Section" of the instruction manual to isolate problems and determine the cause of failures.

6. REM MODEL 642 CHEMILUMINESCENT NO-NO$_x$-NO$_2$ ANALYZER

(a) Replace Teflon element of the sample air filter as required by particulate loading in the area of the monitoring site (at least once/month).

(b) Clean the instrument and flush with nitrogen at 30-day intervals.

(c) Replace drierite dessicant as required.

(d) Rejuvenate catalytic converter when efficiency of conversion drops below 95%.

(e) Refer to the "Troubleshooting Section" of the instruction manual to isolate problems and to determine the cause of failures.

7. MELOY MODEL SA-185R FLAME PHOTOMETRIC TOTAL SULFUR ANALYZER

(a) Replace Teflon element of the sample air filter as required by the particulate loading in the area of the monitoring site (at least once/month).

(b) Replace vacuum pump as required to maintain the required flow rate through the gas flow system.

(c) Clean and maintain the air filter unit for the ventilating fan and oil the circulating fan motor twice each year.

(d) Clean and maintain the burner chamber as prescribed in the instruction manual after 6 months of continuous operation, or sooner if required.

(e) Replace the dilution air orifice (#18 hypodermic needle 1.00 inch long) and the rubber septum as required.

(f) Refer to the "Troubleshooting Section" of the instruction manual to isolate problems and determine the cause of failures.

8. BENDIX MODEL 8300 FLAME PHOTOMETRIC TOTAL SULFUR ANALYZER

(a) Replace Teflon element of the sample air filter as required (at least once/month).

(b) Replace hydrogen cylinder when cylinder pressure decreases to 100 psig, if used.

(c) Replace the hydrogen drier every second cylinder change and/or sooner, if required.

(d) Check reed values if pump performance degrades to the point that it will not maintain the proper sample flow rate.

(e) Refer to the "Troubleshooting Section" of the instruction manual to isolate problems and determine the cause of failures.

9. BECKMAN MODEL 6800 AIR QUALITY CHROMATOGRAPH (THC, CH_4, CO) ANALYZER

(a) Replace the ambient air filter element at least once/month.

(b) Replace all supply air and hydrogen gas driers and filters at six-month intervals, or sooner if required.

(c) Check tightness of all gas line connections on a monthly basis, especially the hydrogen line.

(d) Check tightness of all terminal board connections at six-month intervals.

(e) Clean interior of instrument of dust and accumulated dirt as required.

(f) Verify proper gas flow rates and instrument performance by checking flow rates and running manual chromatograms to verify proper retention times on a weekly basis.

(g) Refer to the "Troubleshooting Section" of the instruction manual to isolate problems and to determine the cause of failures.

10. BENDIX MODEL 8201 AMBIENT HYDROCARBON ANALYZER

(a) Maintenance requirements are not specified in the preliminary instrument manual provided with the analyzer. Good practice dictates replacement of the filter element (preferably Teflon) of the sample inlet filter as required (at least once/month).

(b) Replace the hydrogen cylinder, if used, when the cylinder pressure decreases to 100 psig. Replace gas drier at six-month intervals or sooner, if required.

(c) Clean instrument of dust and accumulated dirt, as required.

(d) Refer to the "Troubleshooting Section" of the instruction manual to isolate problems and to determine the cause of failures.

11. BENDIX MODEL 8501-5FA CARBON MONOXIDE ANALYZER

(a) Inspect the input sample filter on a weekly basis and drain any condensate. Replace the microfilter element at least once/month.

(b) Inspect the gas filter monthly and replace at six-month intervals.

(c) Perform maintenance on the sample pump as required. Foreign particles under the reed valves can be the cause of degradation of pump performance.

(d) Maintain interior of instrument as dust free as possible.

(e) Refer to the "Troubleshooting Section" of the instruction manual to isolate problems and determine the cause of failures.

12. ANDROS MODEL 7000 DUAL ISOTOPE FLUORESCENCE CARBON MONOXIDE ANALYZER

(a) Normal maintenance requires only replacement of the inlet filter element and maintaining the fan filter on the rear panel at periodic intervals (at least once/month).

(b) Refer to the "Troubleshooting Section" of the instruction manual to isolate problems and to determine the cause of failures.

13. TRACOR MODEL 270-HA GAS CHROMATOGRAPHIC-FLAME PHOTOMETRIC ANALYZER

(a) Replace the ambient air filter element and inspect and clean the dilution flow filter on a monthly basis.

(b) Replace all supply gas driers and filter at six-month intervals, or sooner if required.

(c) Check tightness of all gas line connections on a monthly basis, especially the hydrogen line.

(d) Check tightness of all terminal board connections at six-month intervals.

(e) Clean interior of instrument of dust and accumulated dirt as required.

(f) Verify proper gas flow rates and instrument performance by checking flow rates and running manual chromatograms to verify proper retention times on a weekly basis.

(g) Refer to the "Troubleshooting Section" of the instruction manual to isolate problems and to determine the cause of failures.

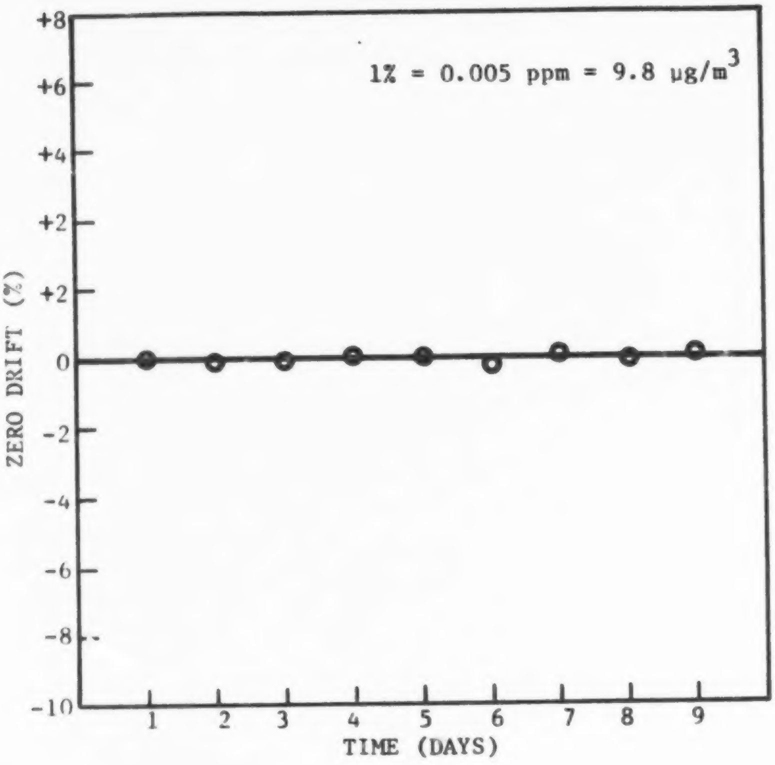
APPENDIX D

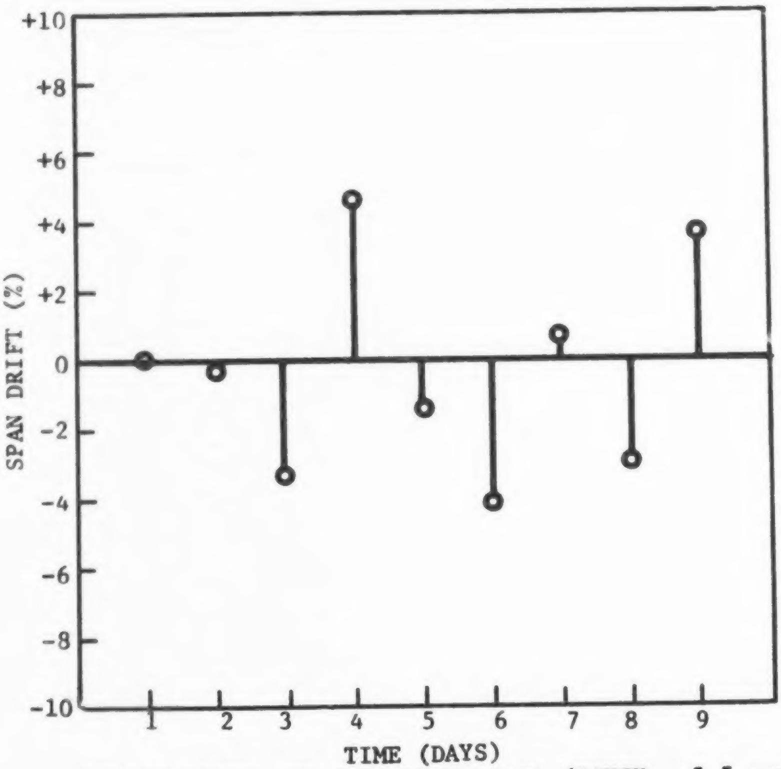
GRAPHICAL PRESENTATION OF ZERO AND SPAN DRIFT

APPENDIX D GRAPHICAL PRESENTATION OF ZERO AND SPAN DRIFT

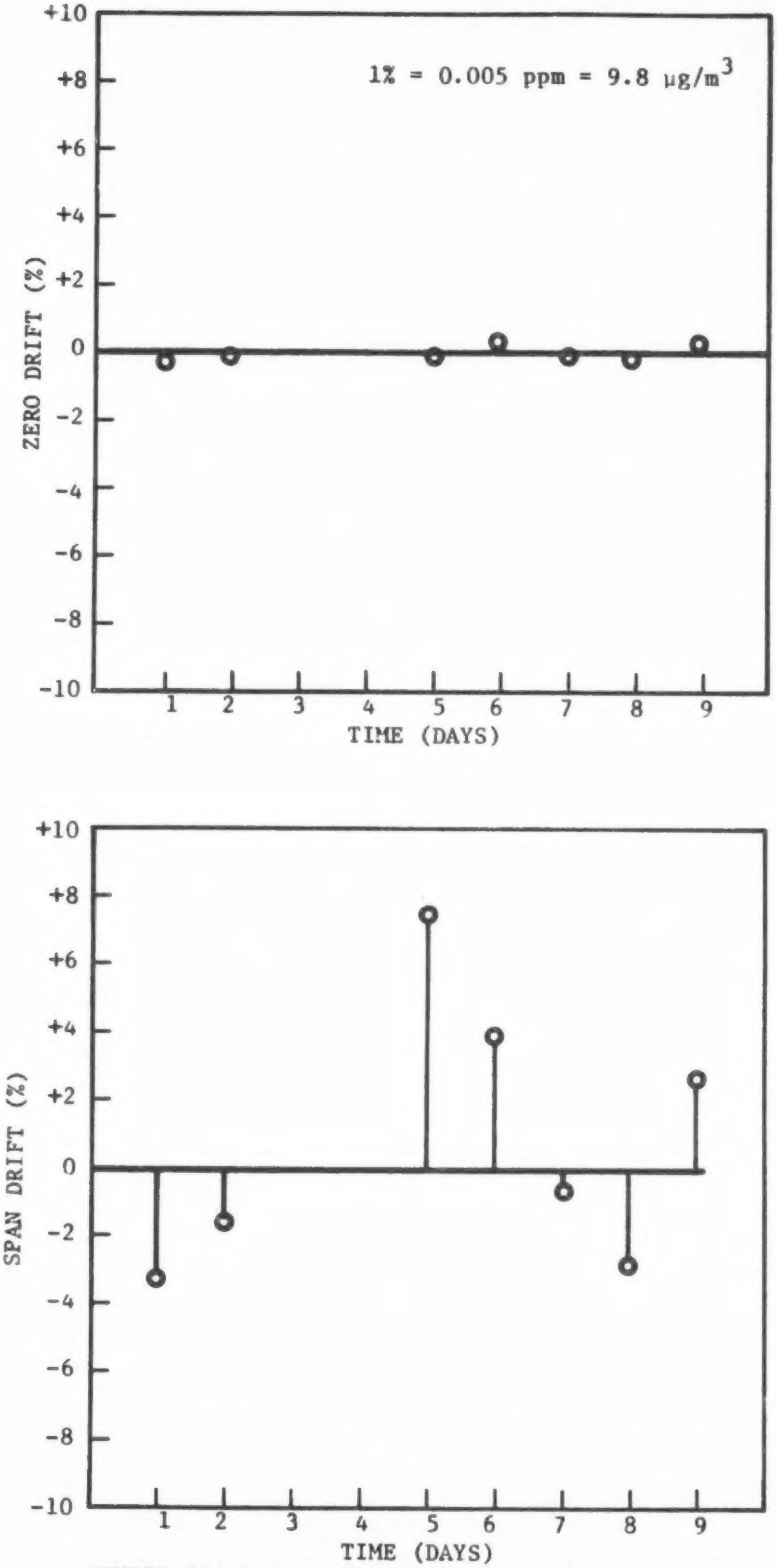
The performance test for stability was conducted as outlined in Section 5.2.1. The following data show zero and span drift in percent of full scale from consecutive calibrations obtained on a daily basis excluding weekends and holidays.

Each of the small circles on the graphs represents a complete multipoint calibration and the drift occurring since the previous calibration. A deletion of several days indicated by a broken time axis indicates the absence of calibrations and an unadjusted operation status of the analyzer. The inclusion of more than one graph of drift data for an instrument indicates that either results of long-term drift tests or additional testing after engineering modifications or repairs were performed on the analyzer. Observation of the drift data shows that some analyzers experience about the same percentage daily drift as weekly drift. Most analyzer drift observed was generally random and not unidirectional.

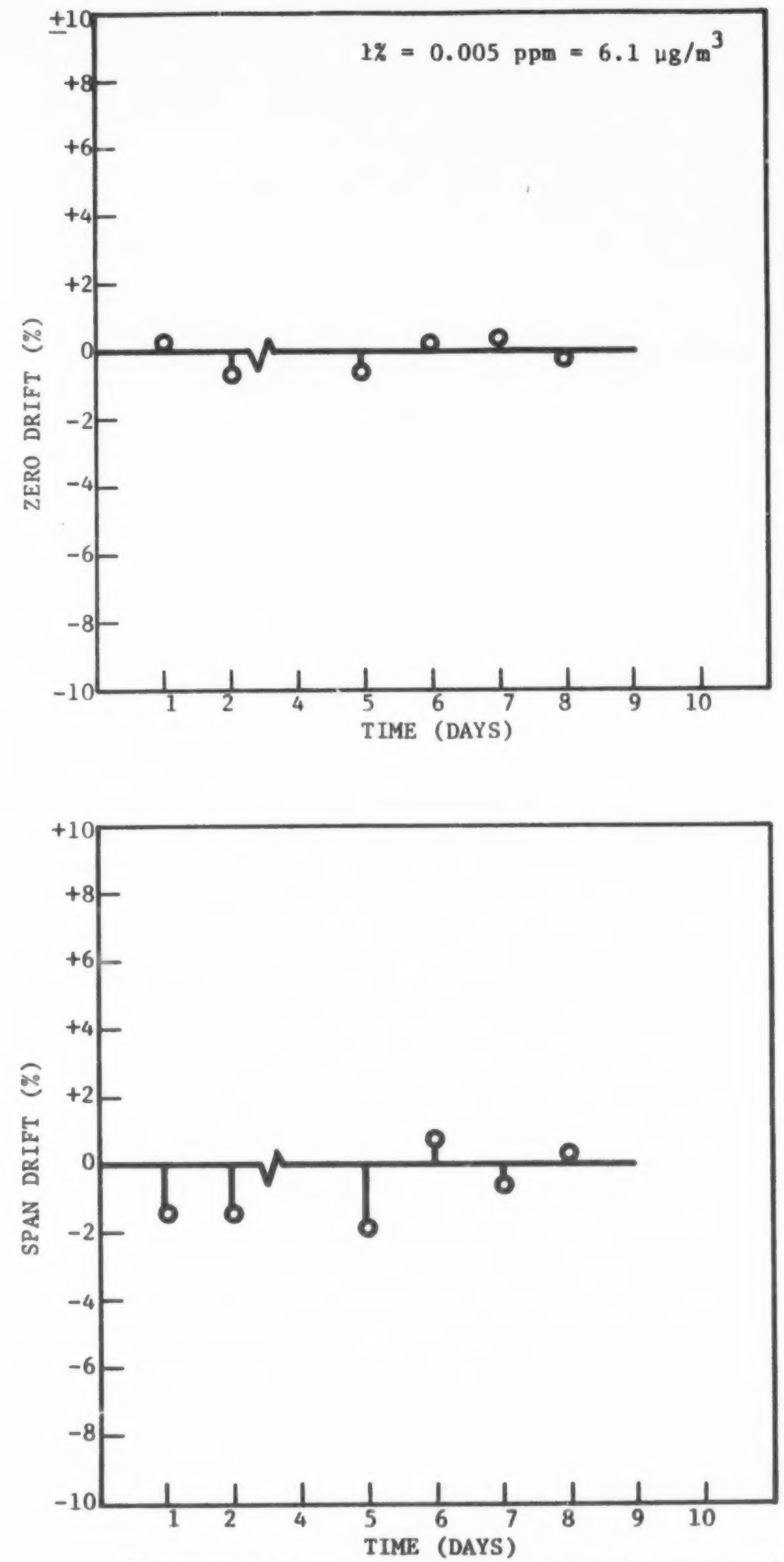




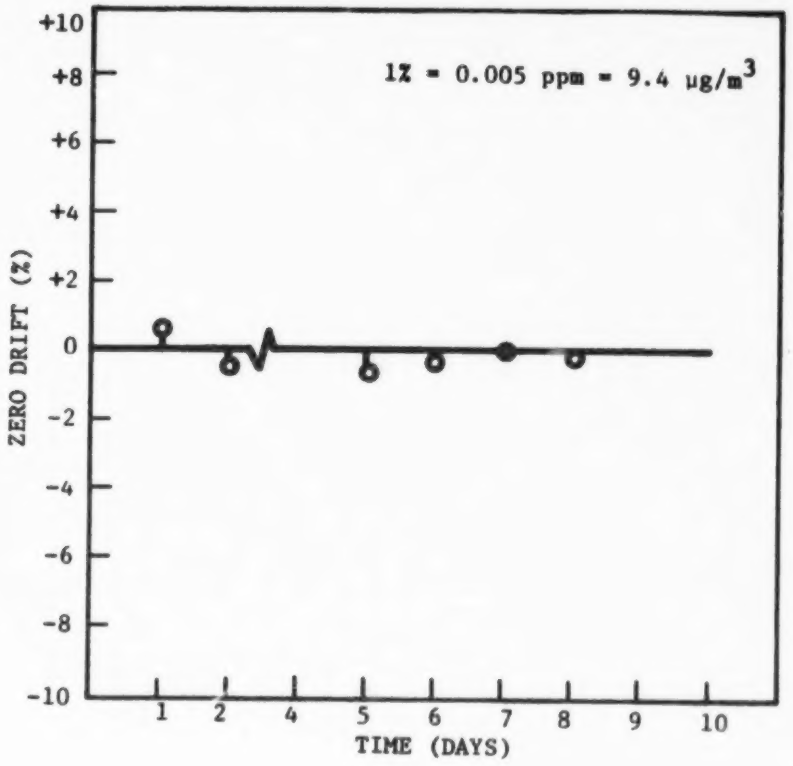
BENDIX OZONE ANALYZER DRIFT DATA (RANGE = 0.5 ppm)

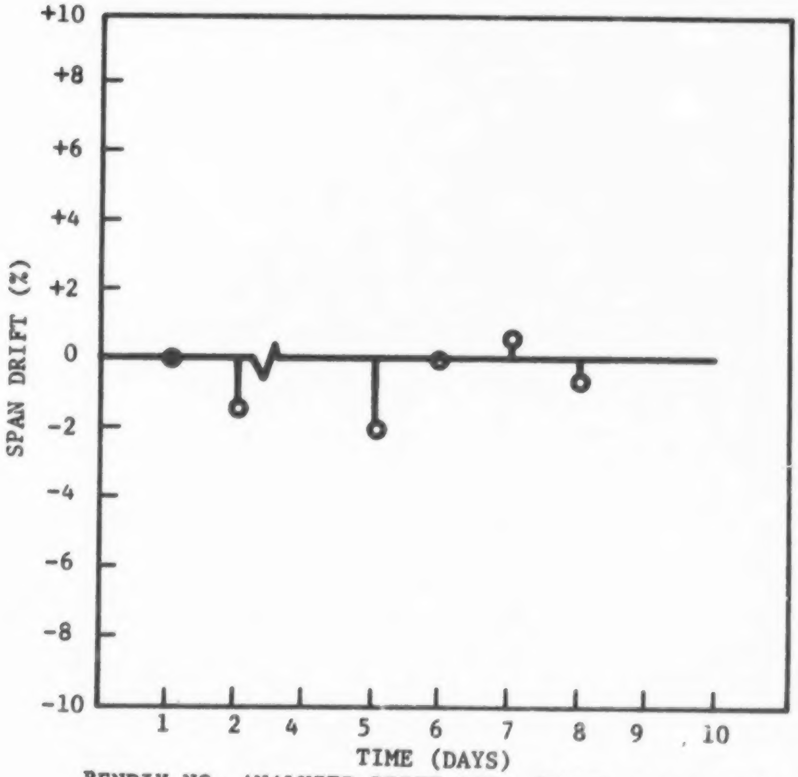


BENDIX OZONE ANALYZER DRIFT DATA (RANGE = 0.5 ppm)

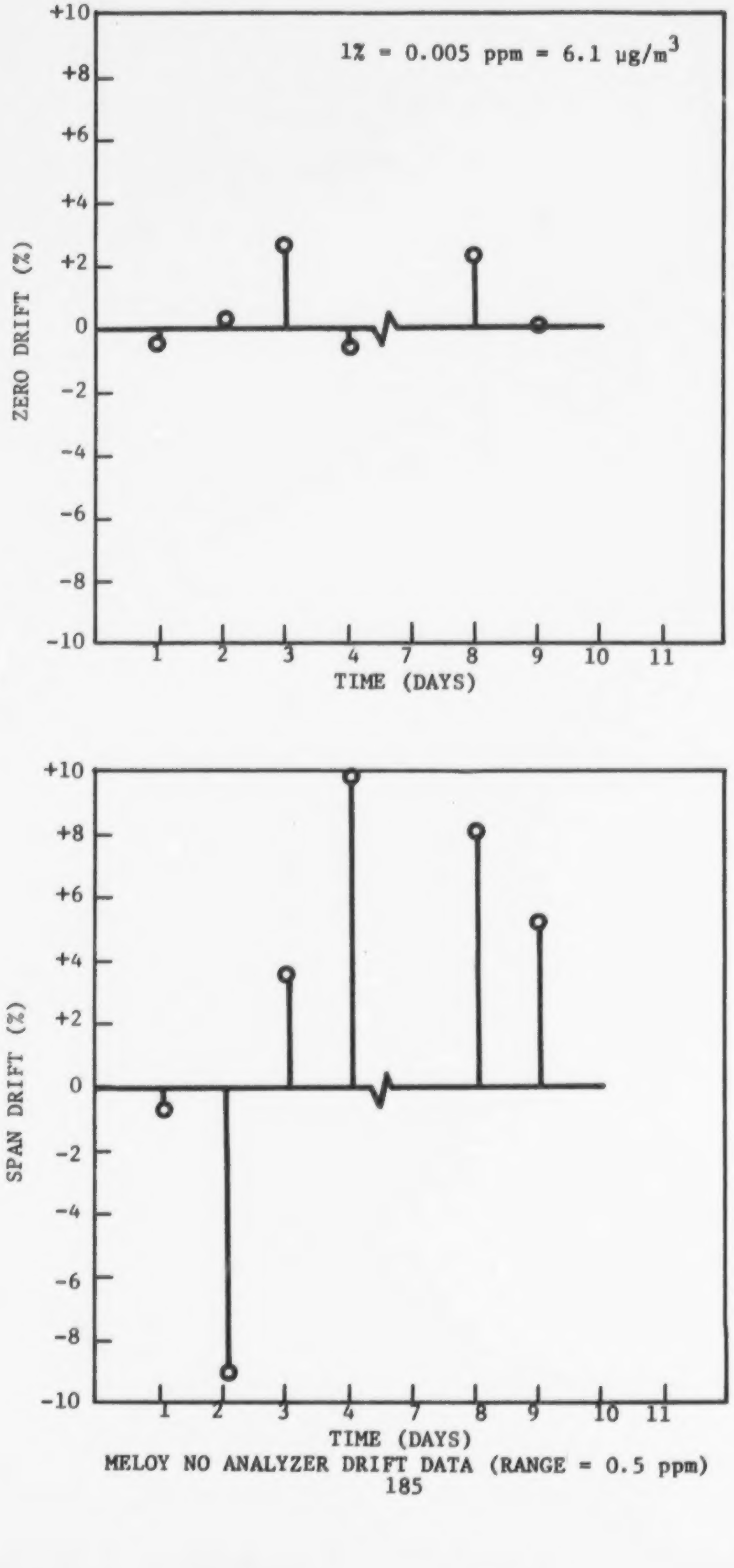


BENDIX NO ANALYZER DRIFT DATA (RANGE = 0.5 ppm)

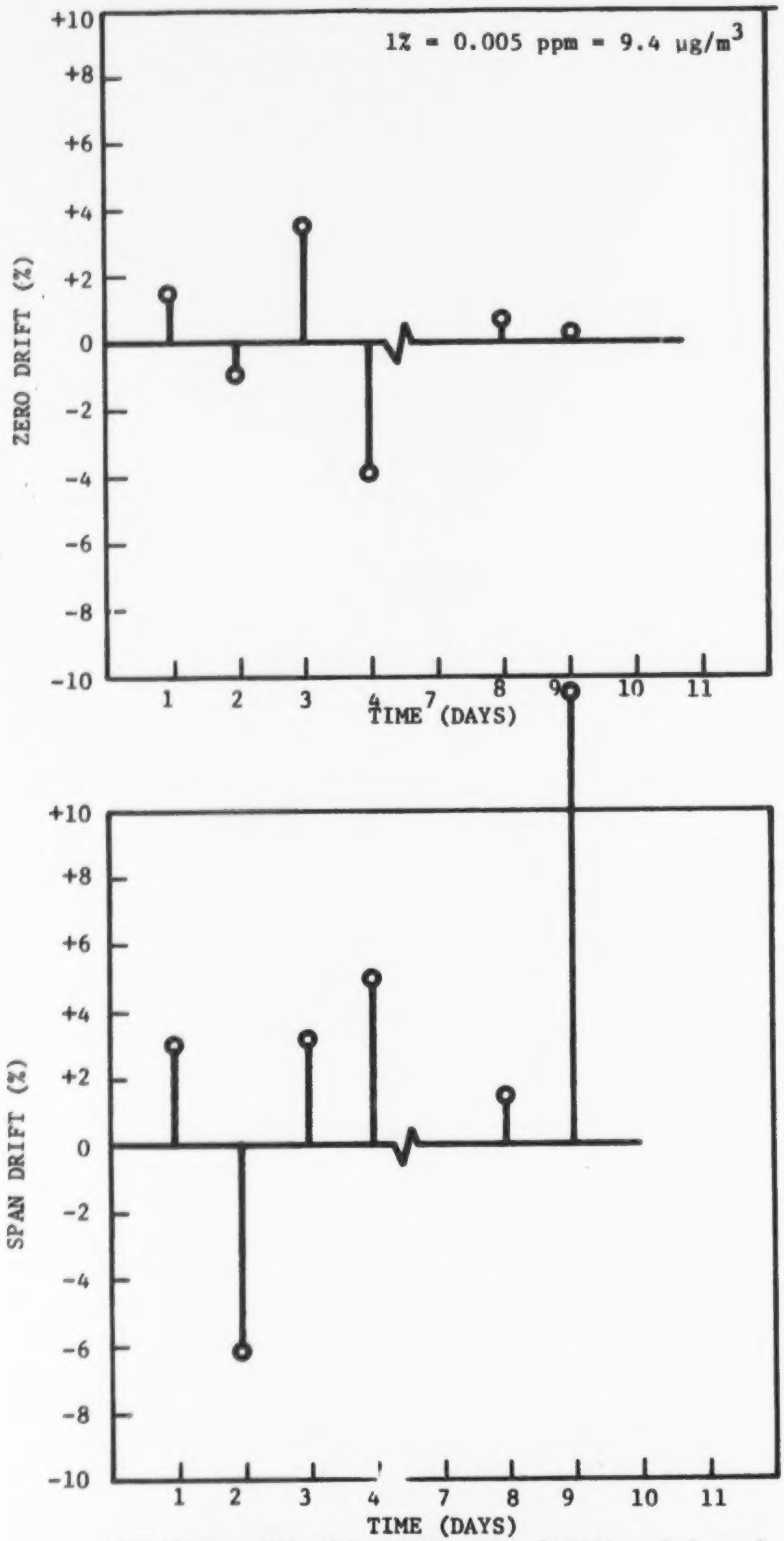




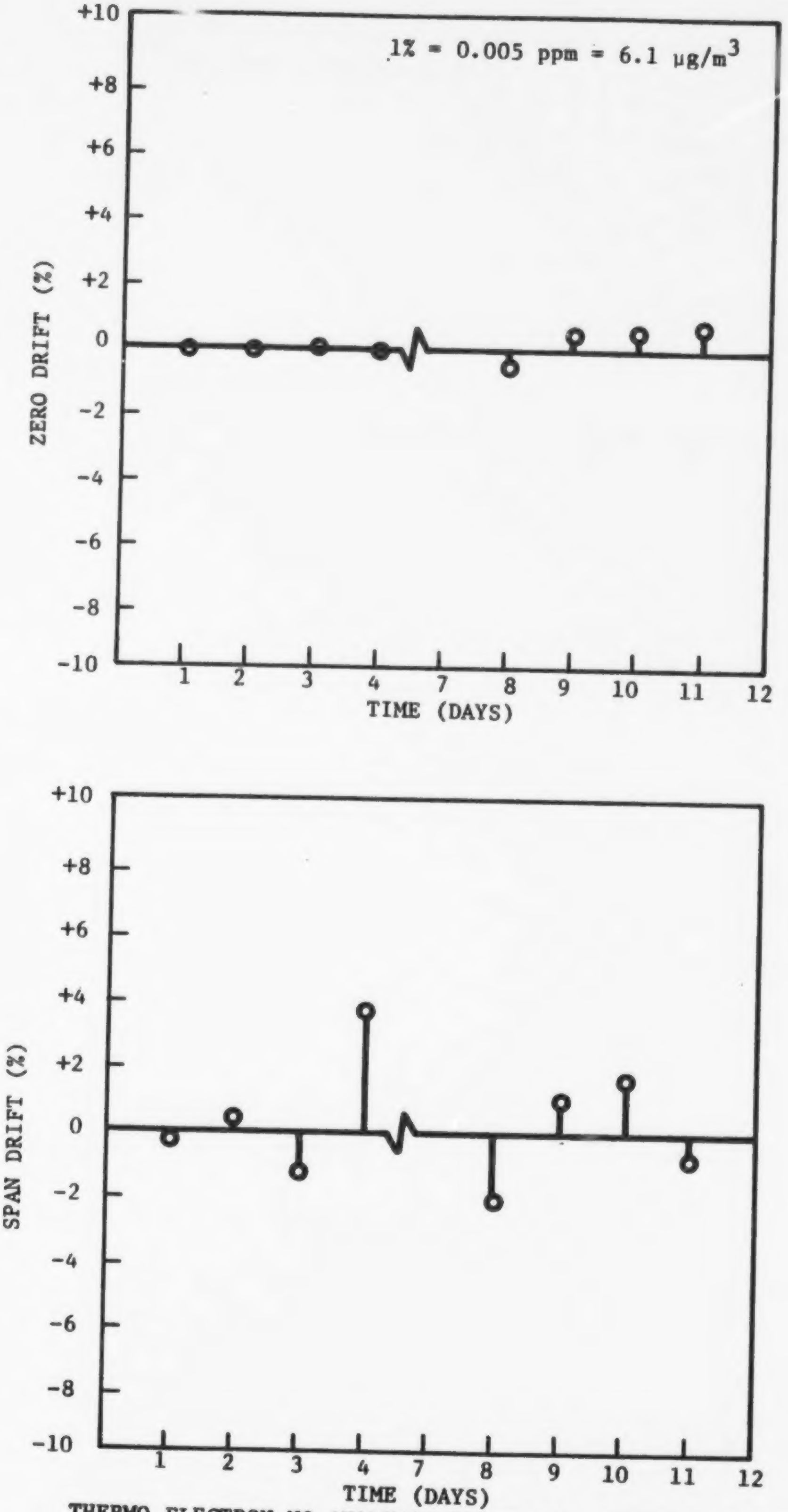
BENDIX NO_2 ANALYZER DRIFT DATA (RANGE = 0.5 ppm)



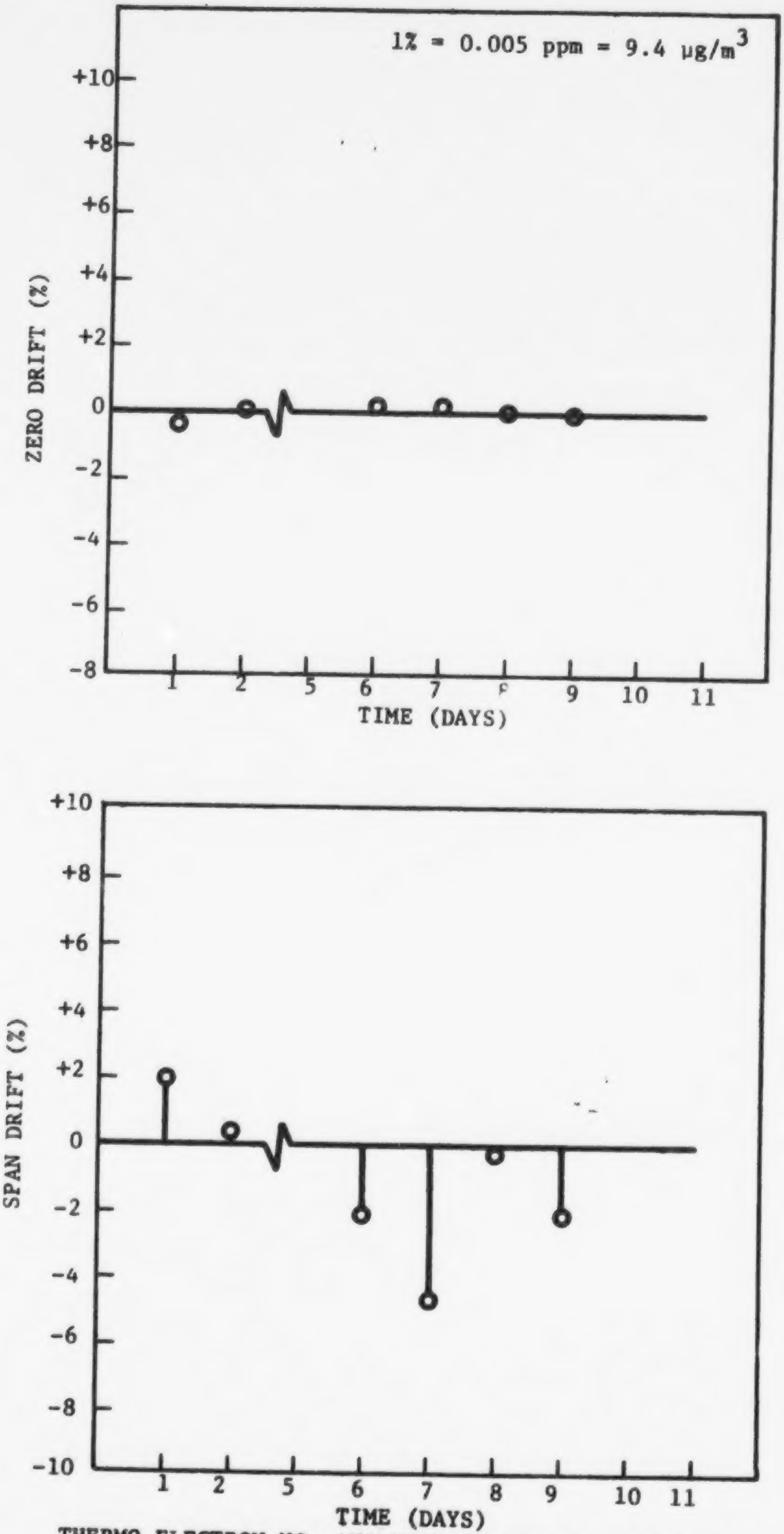
MELOY NO ANALYZER DRIFT DATA (RANGE = 0.5 ppm)



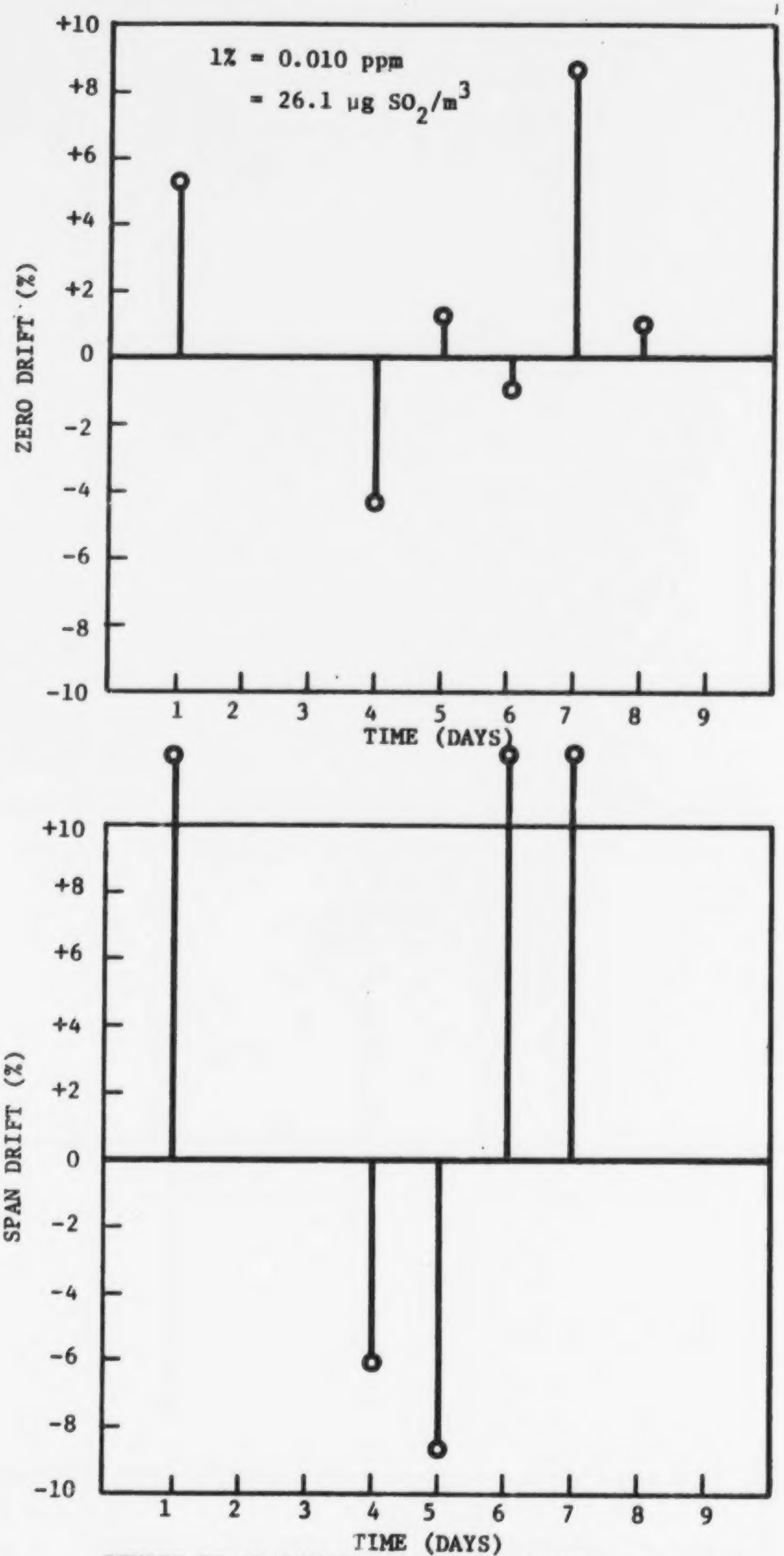
MELOY NO_2 ANALYZER DRIFT DATA (RANGE = 0.5 ppm)



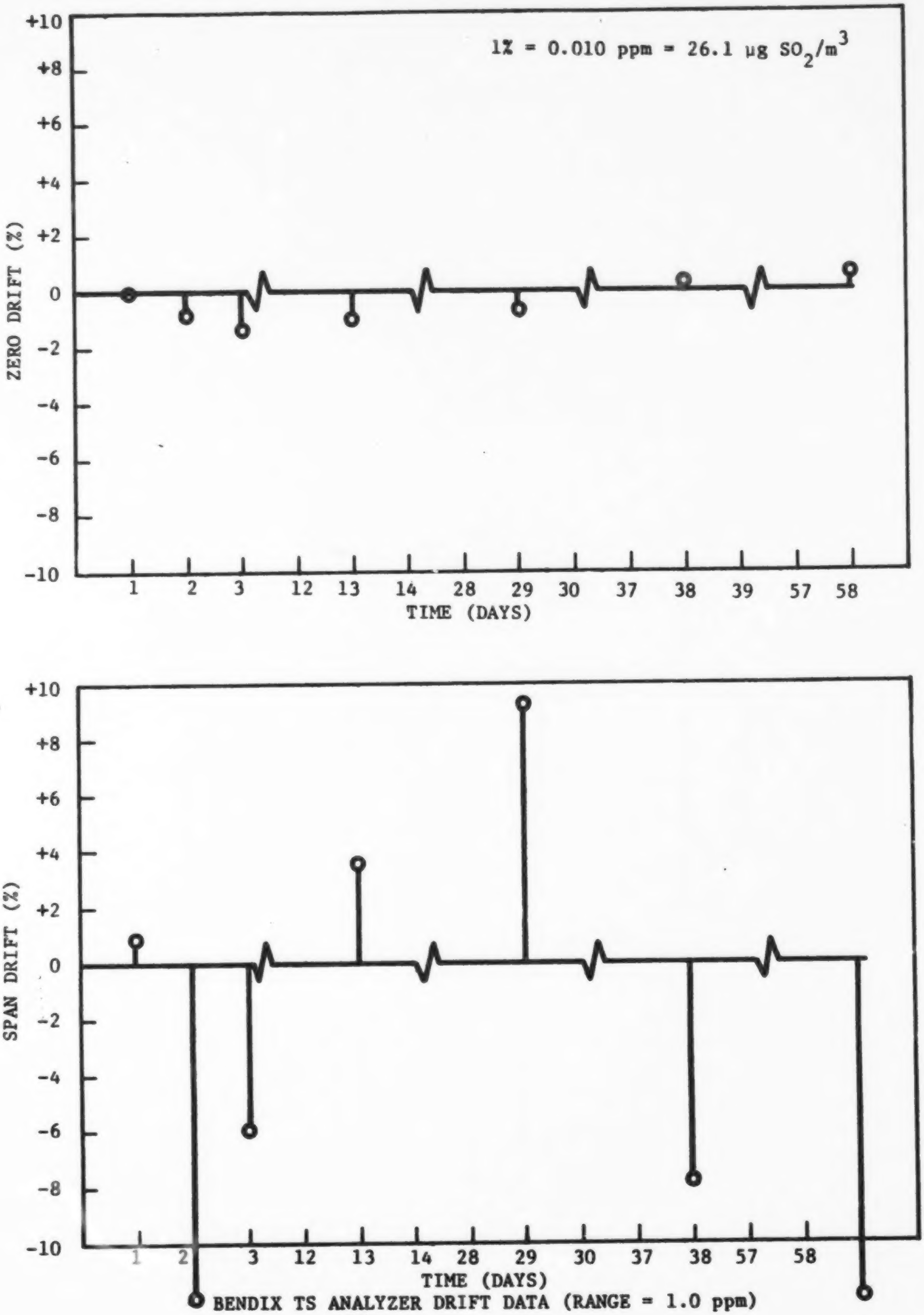
THERMO ELECTRON NO ANALYZER DRIFT DATA (RANGE = 0.5 ppm)



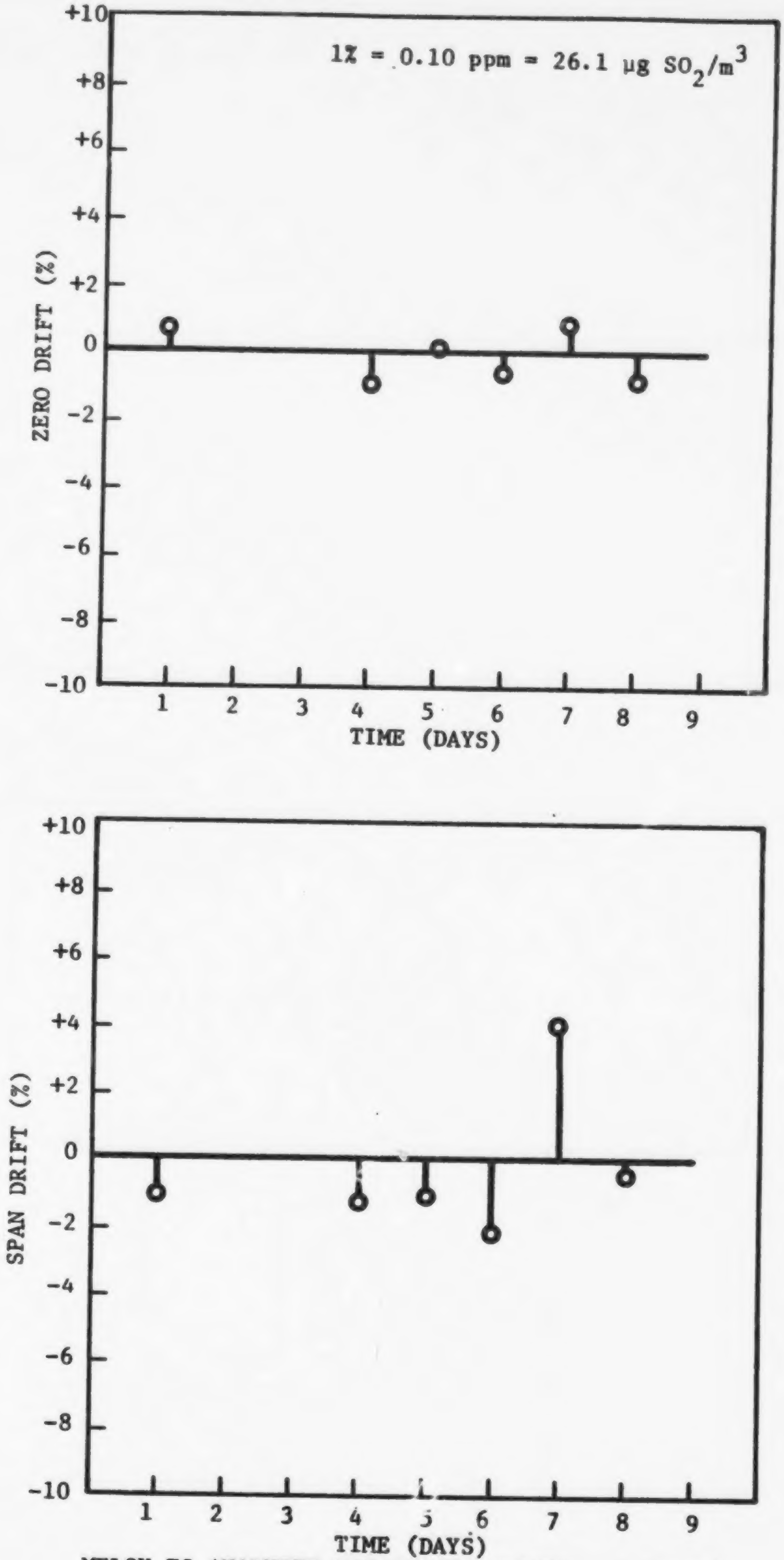
THERMO ELECTRON NO_2 ANALYZER DRIFT DATA (RANGE = 0.5 ppm)



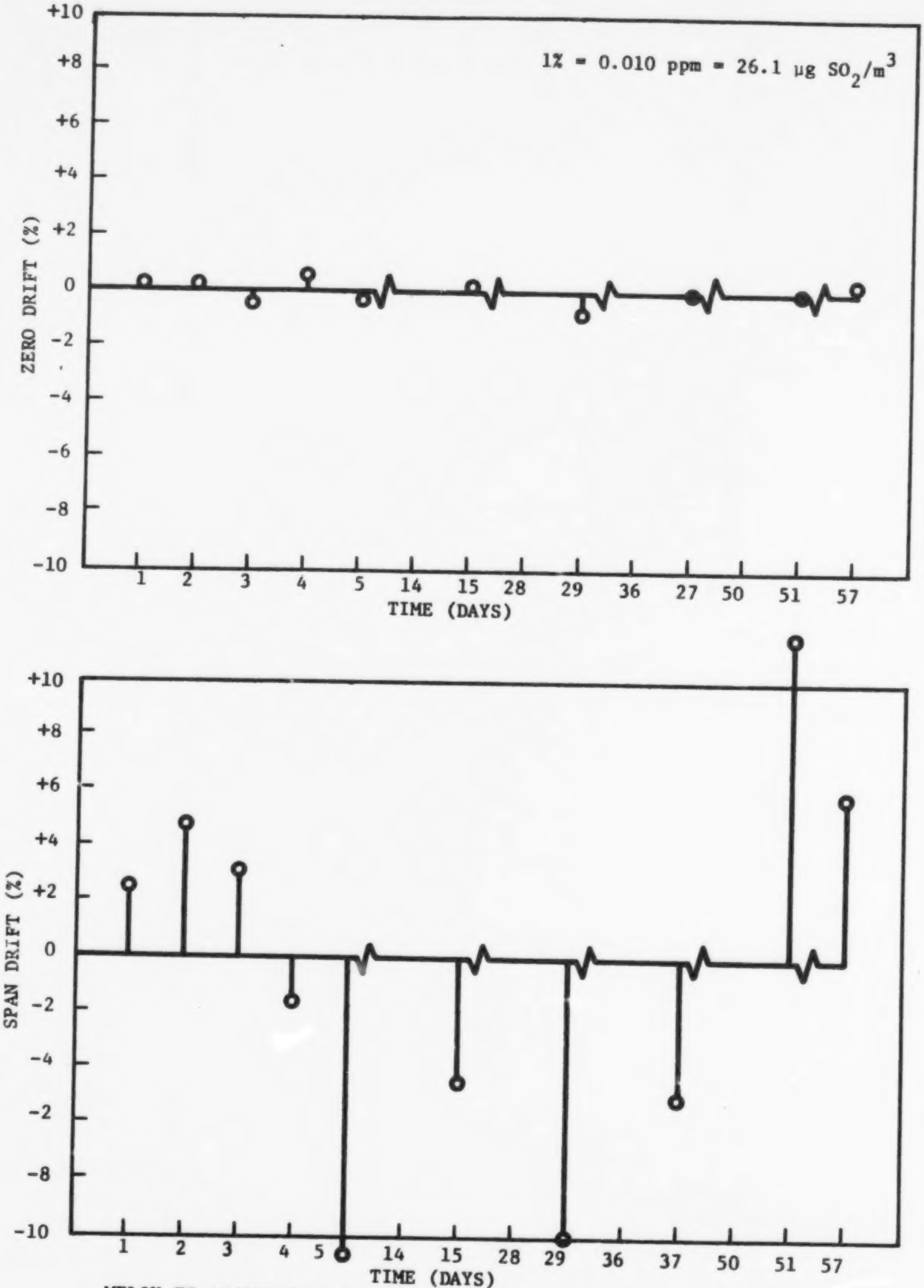
BENDIX TS ANALYZER DRIFT DATA (RANGE = 1.0 ppm)



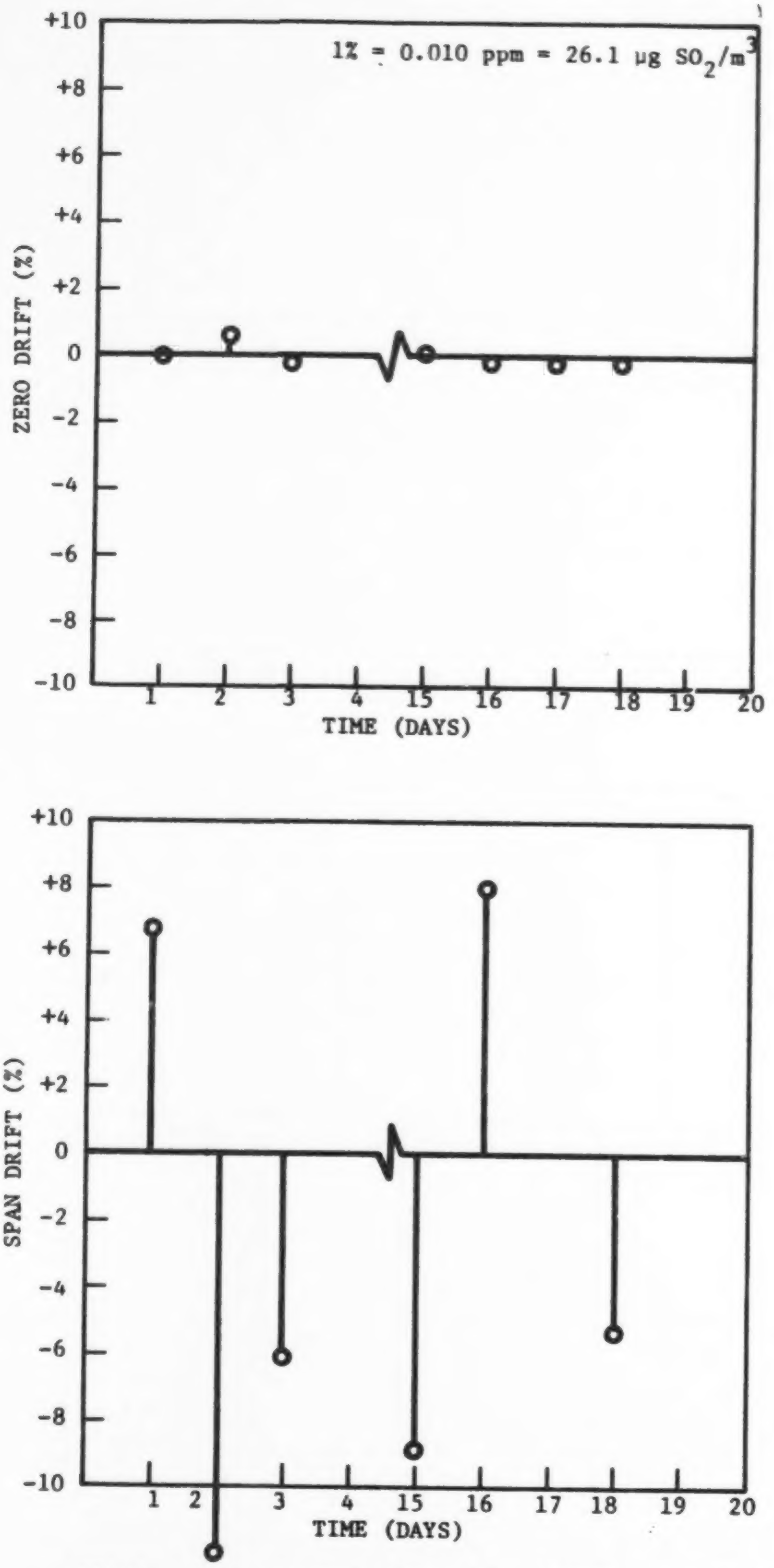
BENDIX TS ANALYZER DRIFT DATA (RANGE = 1.0 ppm)



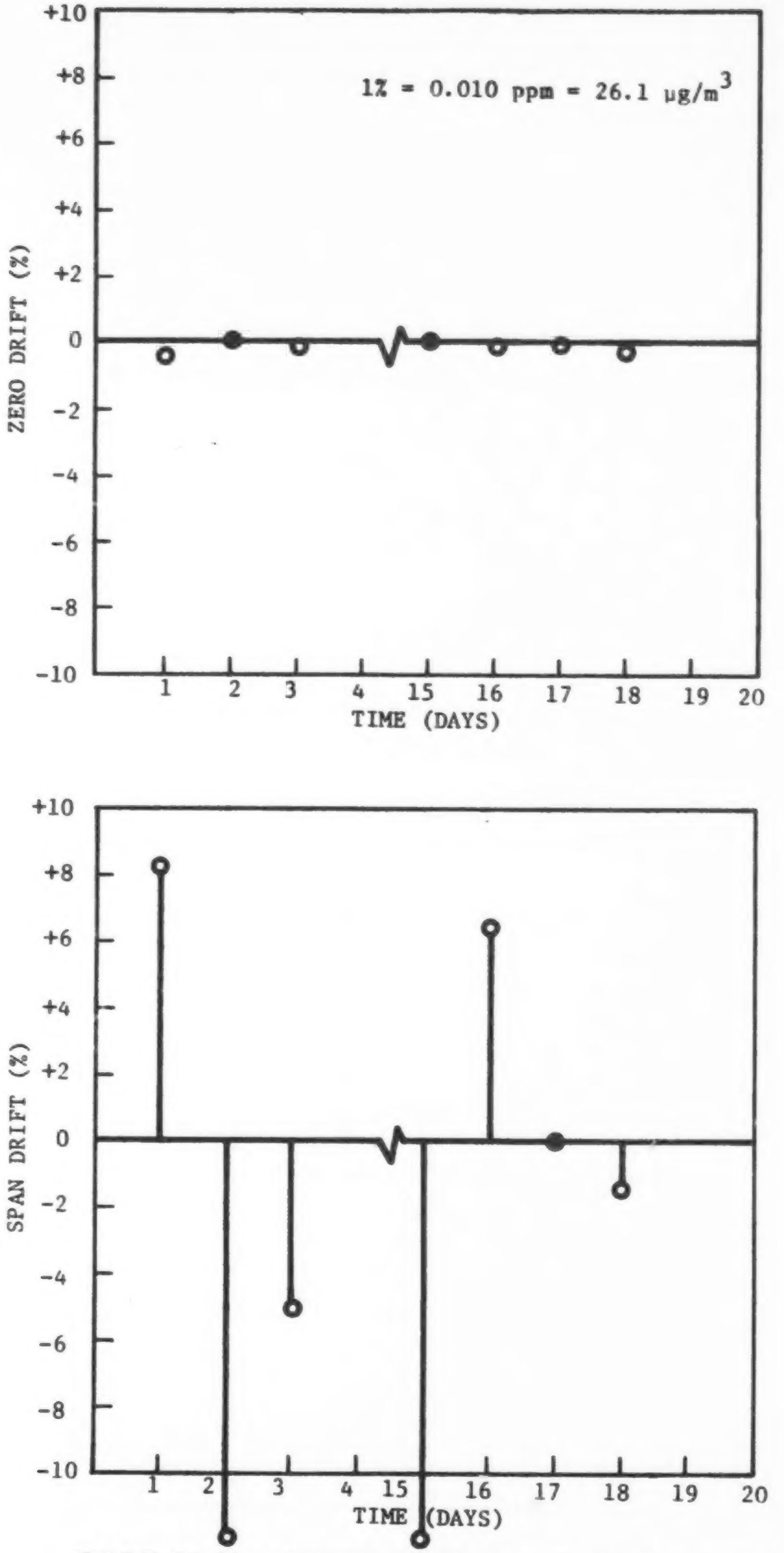
MELOY TS ANALYZER DRIFT DATA (RANGE = 1.0 ppm)



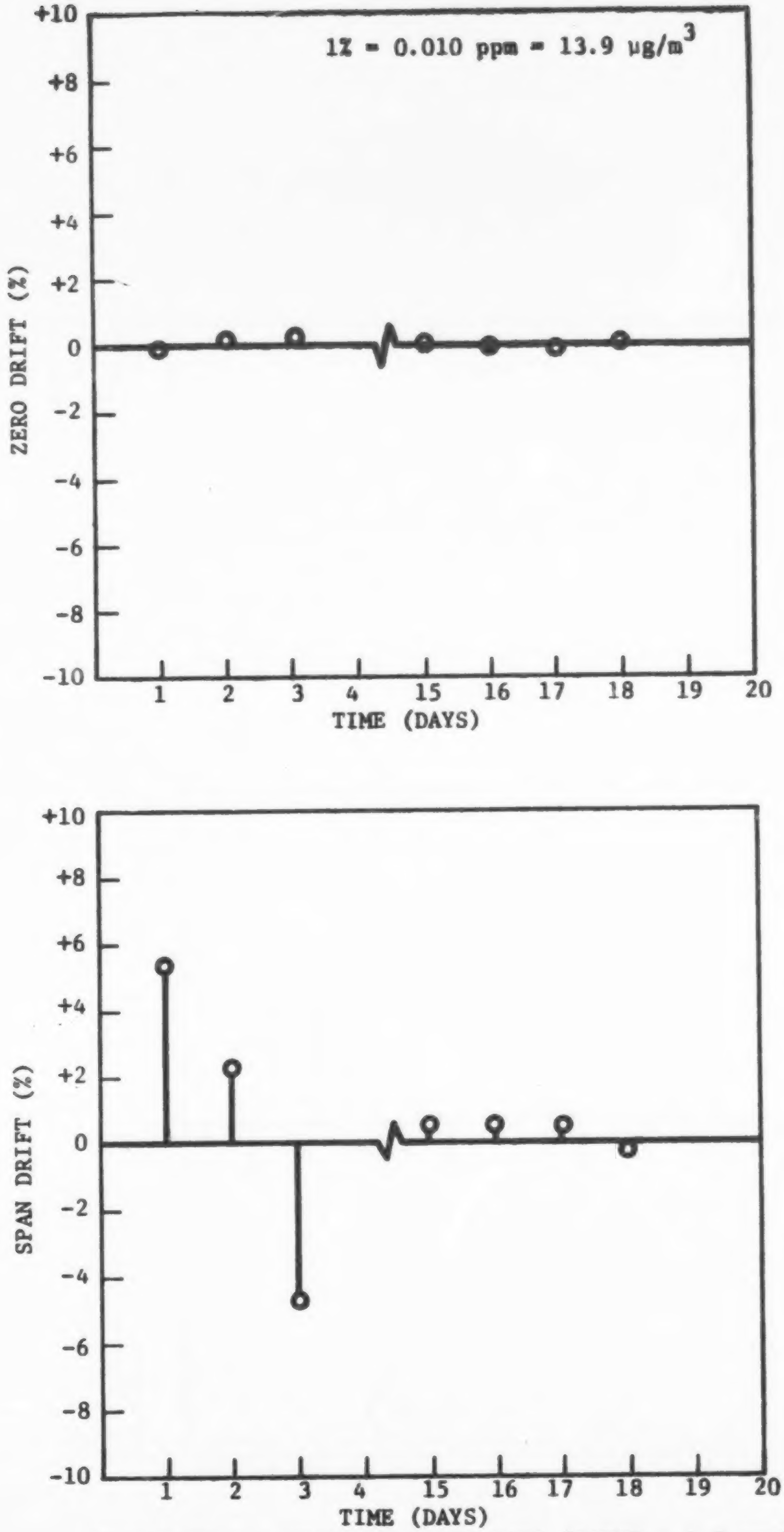
MELOY TS ANALYZER DRIFT DATA (RANGE 1.0 ppm)



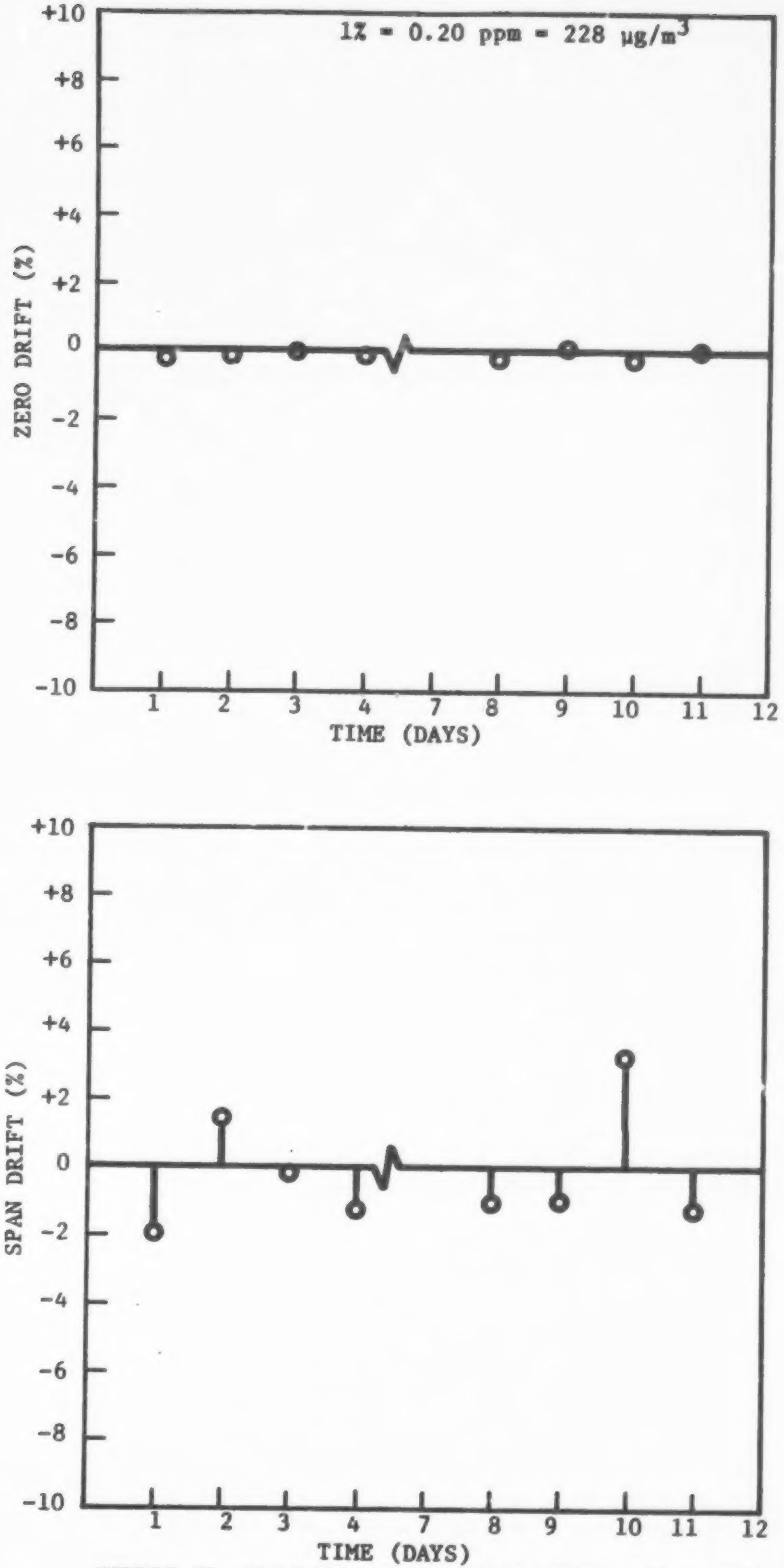
TRACOR GC TS ANALYZER DRIFT DATA (RANGE = 1.0 ppm)



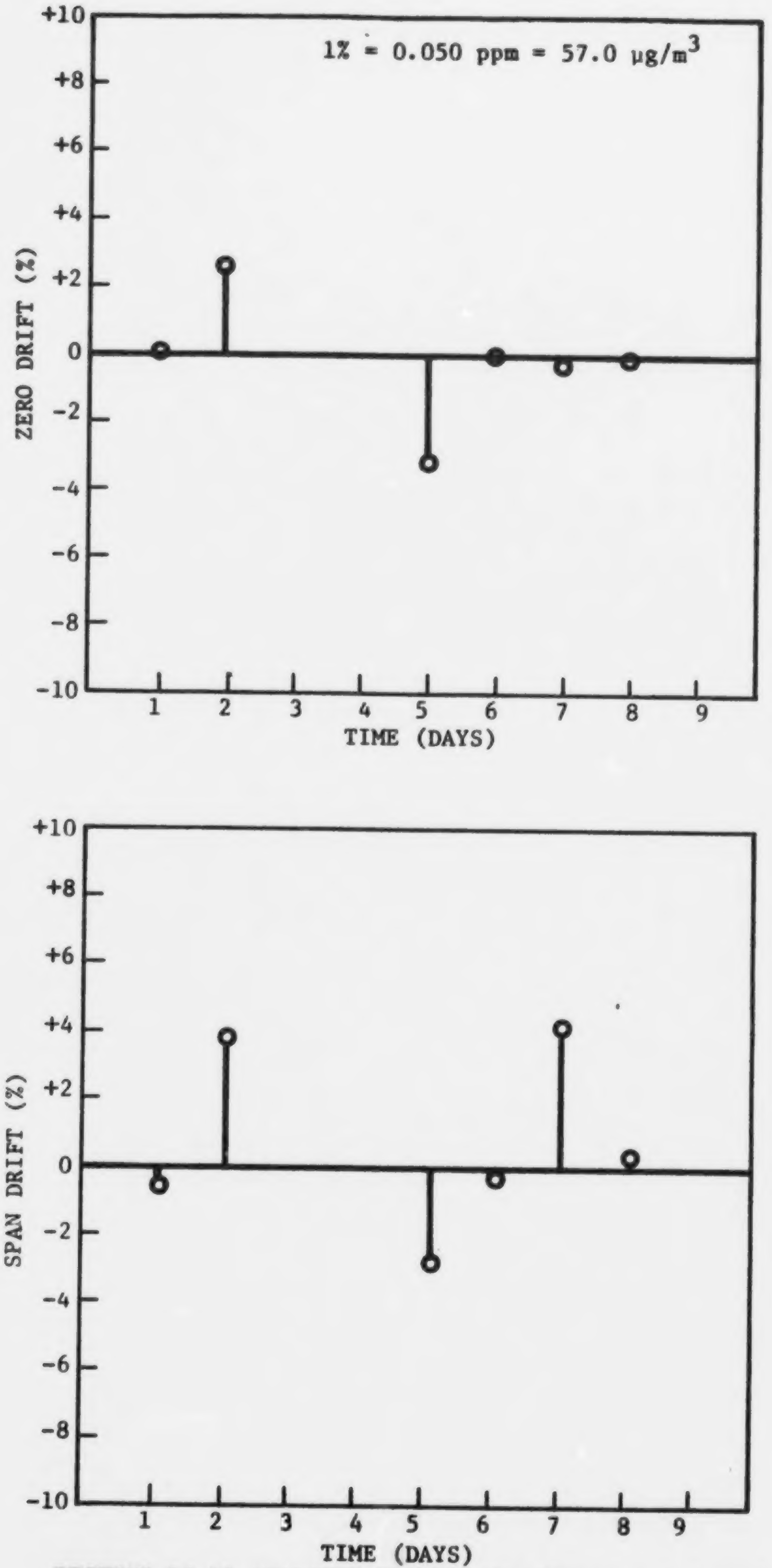
TRACOR GC SO_2 ANALYZER DRIFT DATA (RANGE = 1.0 ppm)



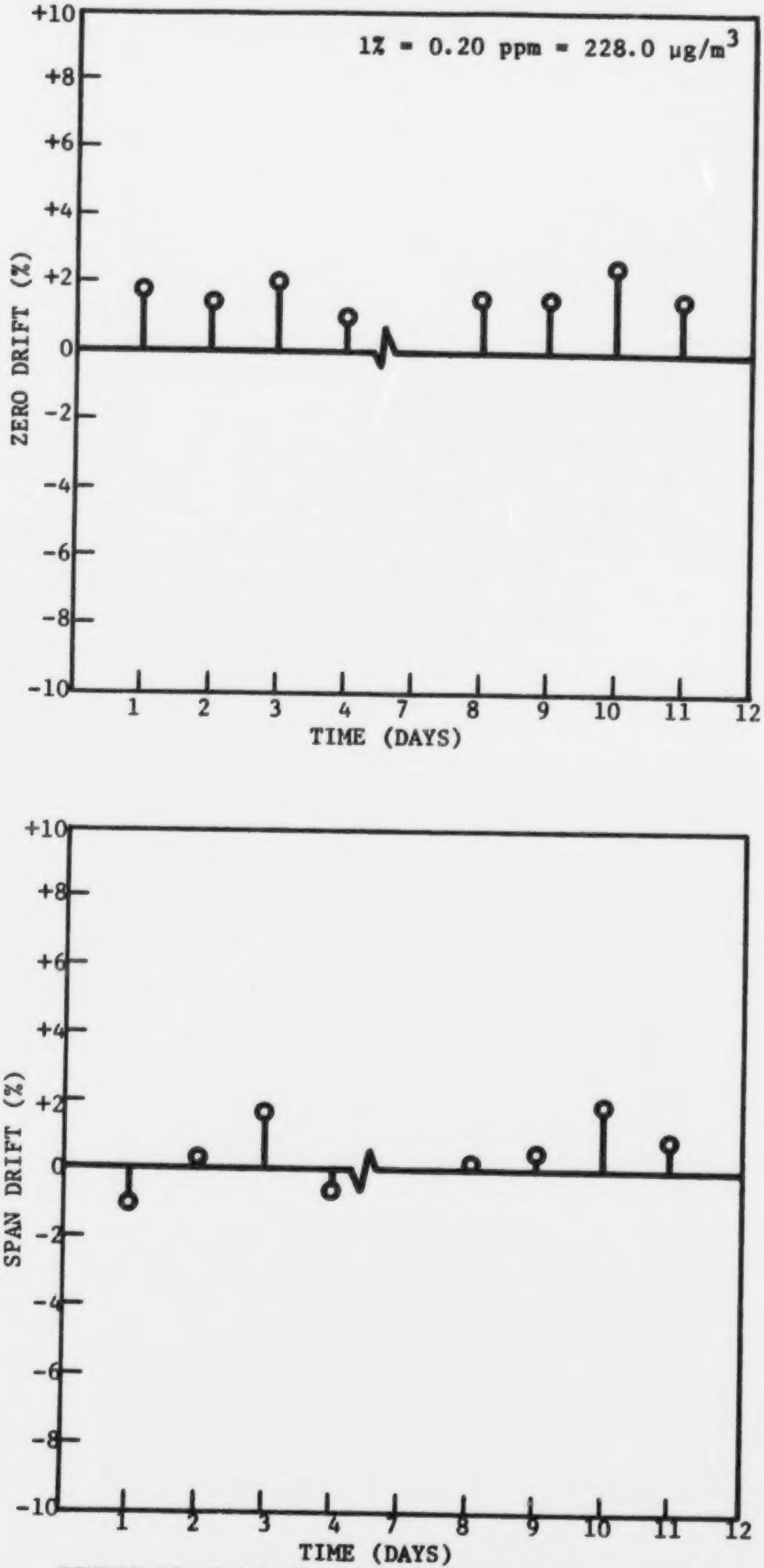
TRACOR GC H_2S ANALYZER DRIFT DATA (RANGE = 1.0 ppm)



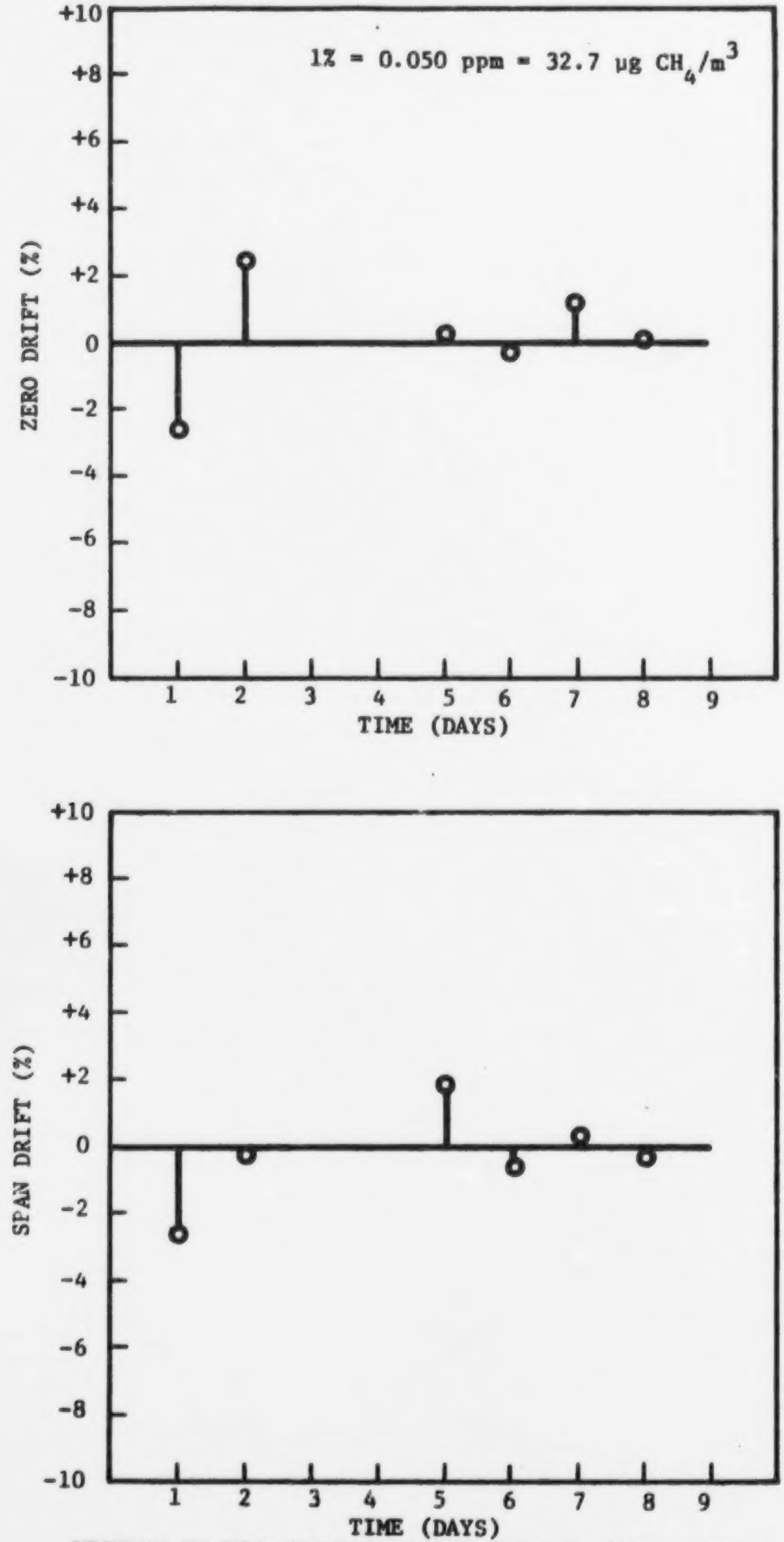
ANDROS CO ANALYZER DRIFT DATA (RANGE = 20.0 ppm)



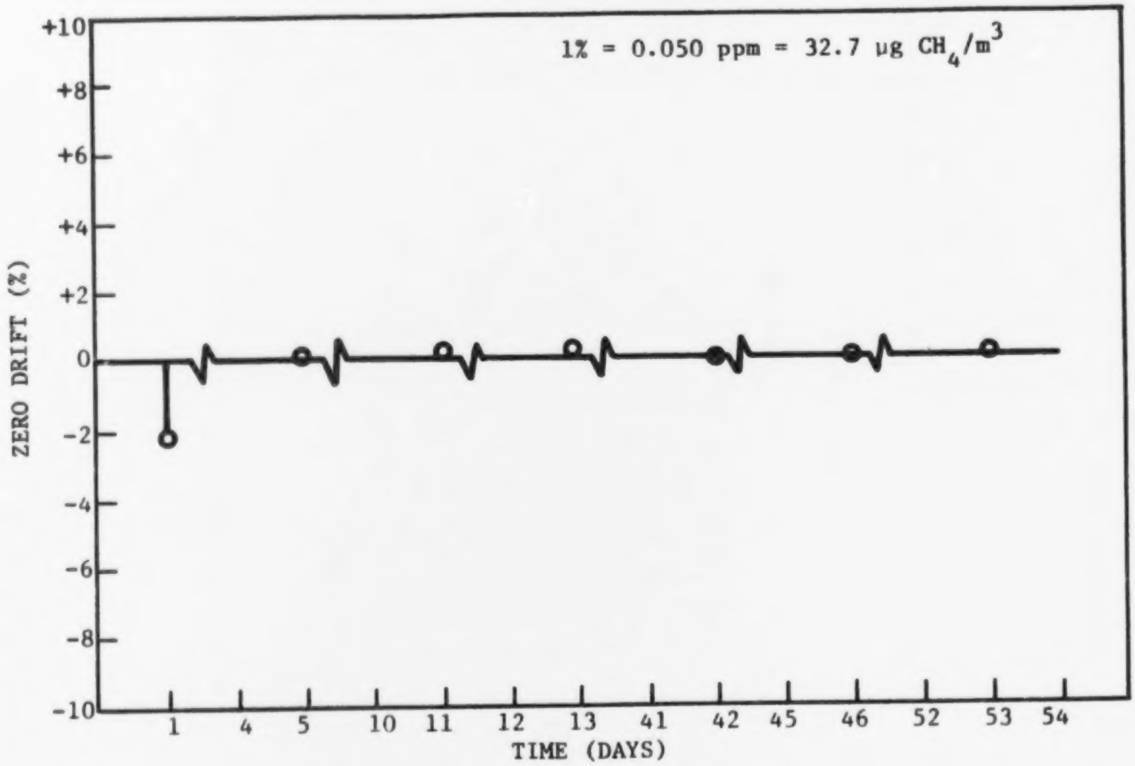
BECKMAN GC CO ANALYZER DRIFT DATA (Range = 5.0 ppm)

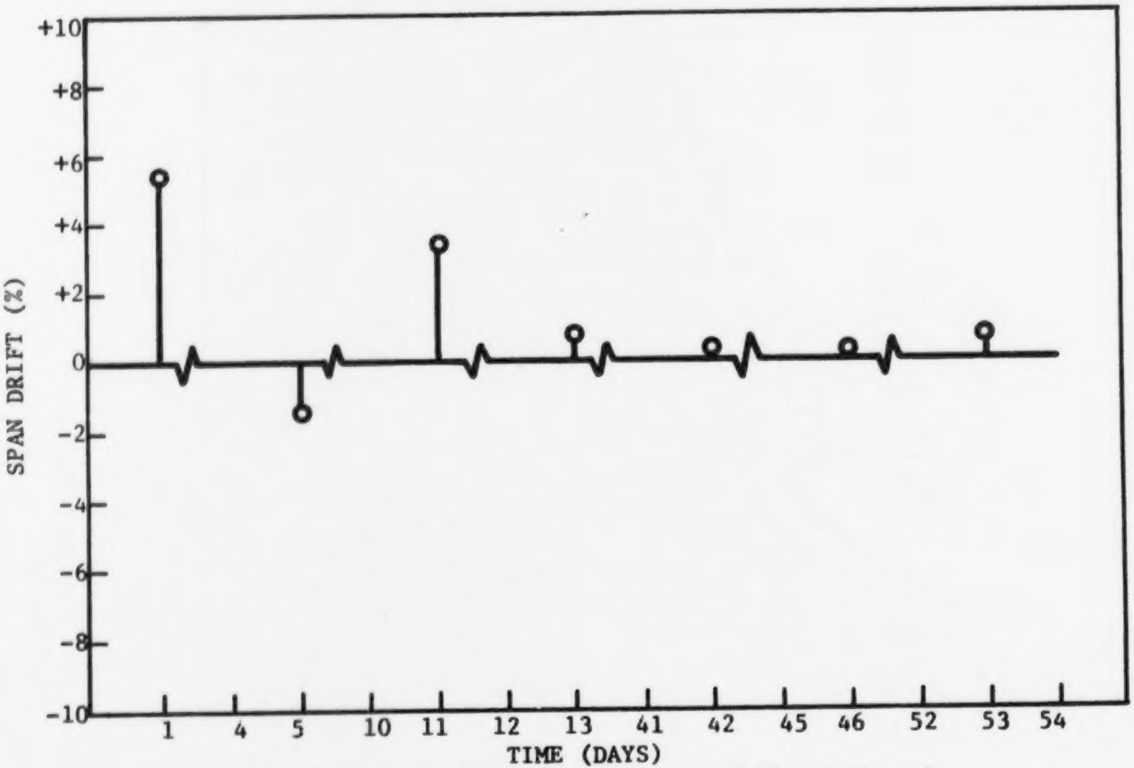


BENDIX CO ANALYZER DRIFT DATA (RANGE = 20.0 ppm)

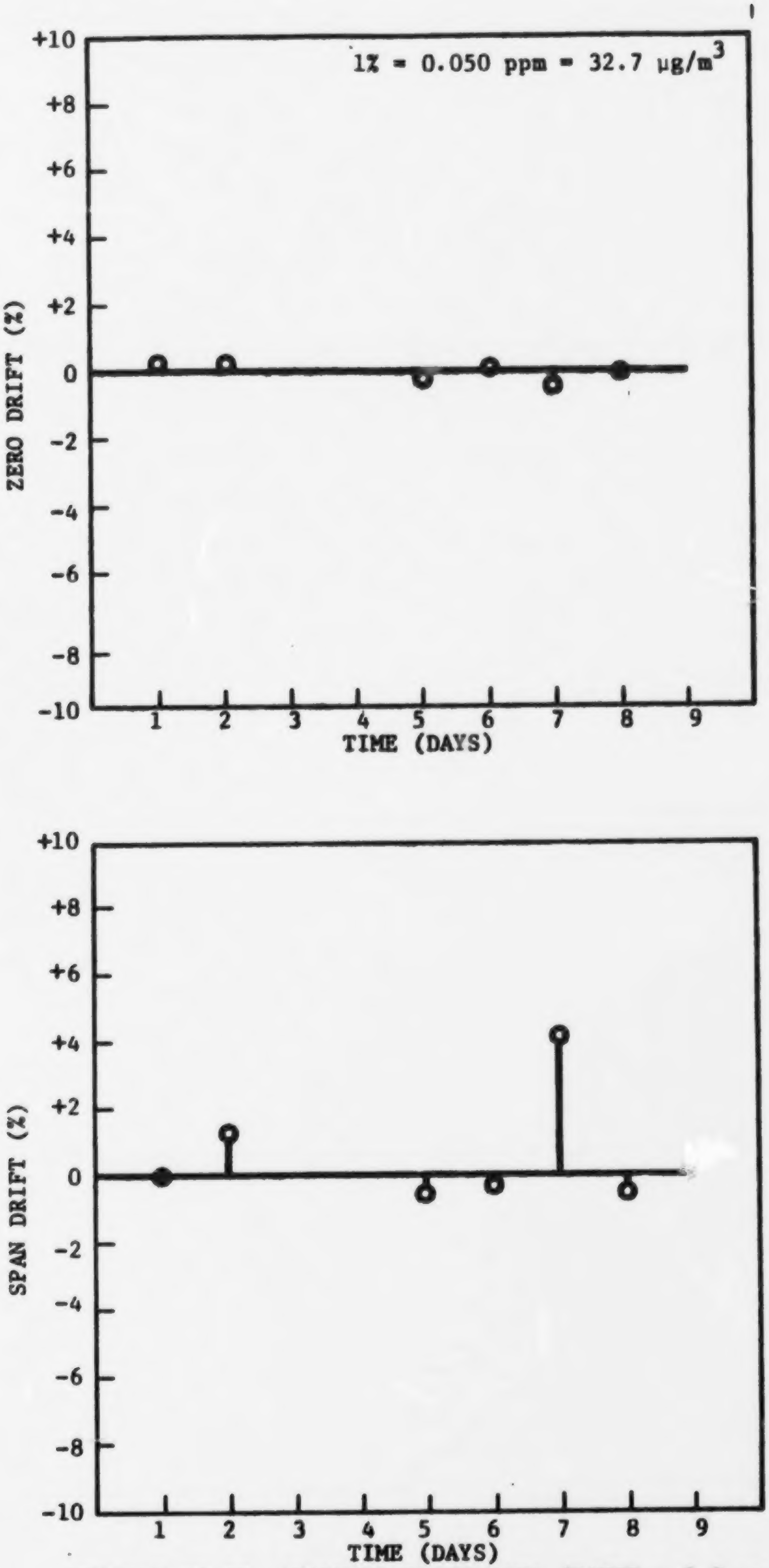


BECKMAN GC THC ANALYZER DRIFT DATA (RANGE = 5.0 ppm)

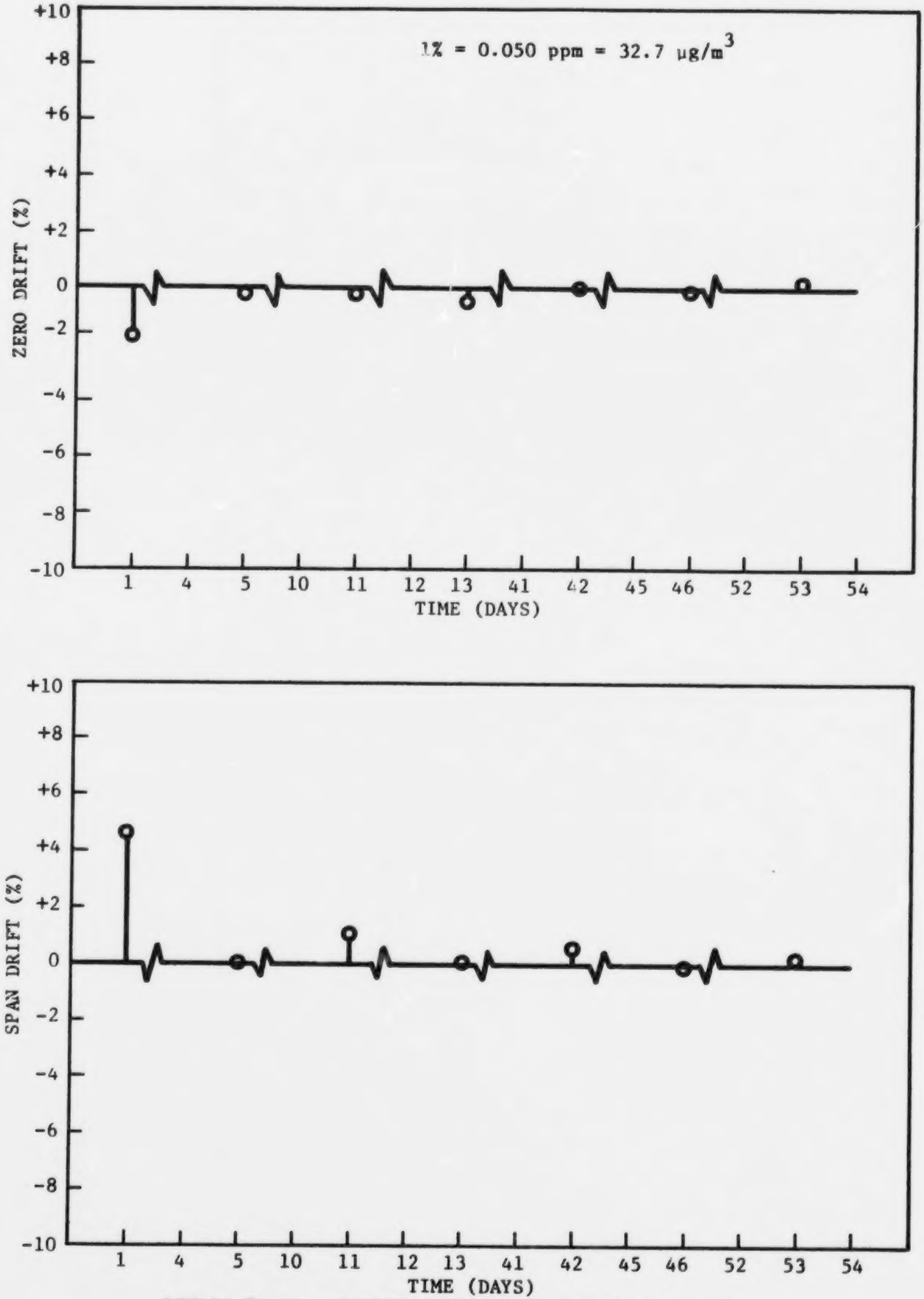




BENDIX GC THC ANALYZER DRIFT DATA (RANGE = 5.0 ppm)



BECKMAN GC CH_4 ANALYZER DRIFT DATA (RANGE = 5.0 ppm)



BENDIX GC CH_4 ANALYZER DRIFT DATA (RANGE 5.0 ppm)

APPENDIX E

SUMMARY OF DATA FORMATS
(HP-COMPUTER OUTPUTS)

```
FEBRUARY 20, 1973        15:20 HOURS
  1    -.105920                     34    .000010
  2    -.105950                     35    .000010
  3    -.000550                     36    .093640
  4    -.002770                     37  -.007300
  5     .004550                     38    .205060
  6     .003040                     39  4.669600
  7     .793650                     40  3.525200
  8     .045270                     41  -.001150
  9     .026620                     42  -.004450
 10    -.744970                     43    .001250
 11    -.108650                     44  -.000870
 12    -.548480                     45  -.000680
 13     .002010                     46  -.105920
 14     .002300                     47  -.895610
 15     .638510                     48  -.896400
 16   15.026998                     49  -.897790
 17  -15.077000                     50  -.106630
 18    -.000450                     51  -.105930
 19    -.002070                     52  -.105970
 20     .000020                     53  -.105950
 21    -.034740                     54  -.610430
 22     .004030                     55  -.106040
 23    -.028810                     56  -.105900
 24     .030690                     57  -.105970
 25     .011160                     58  -.105890
 26     .036540                     59  -.106130
 27     .010750                     60  -.512430
 28    -.024930                     61  -.513720
 29     .003230                     62  -.513350
 30     .045160                     63  -.512640
 31     .003590                     64  -.513900
 32     .003220                     65  -.512690
 33     .023660
```

Printout of Voltages Measured by Data Acquisition System (Long Format)

```
MEL. NO     $$$$$$$$$$ L      PPM
MEL.NO2     $$$$$$$$$$ L      PPM
MEL.NOX     $$$$$$$$$$ L      PPM
BEN. NO          .0131        PPM
BEN.NO2          .0089        PPM
BEN.NOX          .0198        PPM
BEN.O3           .0461        PPM
BEN.SO2          .0013        PPM
TRAC.TS          .0092        PPM
TRAC.H2S         .0000        PPM
TRAC.SO2         .0039        PPM
MEL.SO2          .0043        PPM
BEK.THC          .0389 T      PPM
BEK.CH4         -.0020 T      PPM
BEK.CO           .0830 T      PPM
BEK.THC         4.6034 T      PPM
BEK.CH4         3.9192 T      PPM
BEK.CO          -.0882 T      PPM
DIAL 1/3        -.0033        ROTAT
DIAL 2/4        -.0000        ROTAT
MEL. NO    |     .50000| * X +  |    .00000 |   PPM
MEL.NO2    |     .50000| * X +  |    .00000 |   PPM
MEL.NOX    |     .50000| * X +  |    .00000 |   PPM
BEN. NO    |     .50067| * X +  |   -.00057 |   PPM
BEN.NO2    |     .47600| * X +  |   -.00024 |   PPM
BEN.NOX    |     .49730| * X +  |   -.00013 |   PPM
BEN.O3     |    4.32915| * X +  |    .00104 |   PPM
BEN.SO2    |    2.12518| * X +  |   -.00664 |   PPM
TRAC.TS    |     .18479| * X +  |   -.00050 |   PPM
TRAC.H2S   |     .16929| * X +  |   -.00057 |   PPM
TRAC.SO2   |     .19732| * X +  |   -.00058 |   PPM
MEL.SO2    |     .98331| * X +  |   -.01932 |   PPM
BEK.THC    |     .40000| * X +  |    .00000 |   PPM
BEK.CH4    |     .40000| * X +  |    .00000 |   PPM
BEK.CO     |     .40000| * X +  |    .00000 |   PPM
BEK.THC    |    1.03635| * X +  |   -.20802 |   PPM
BEK.CH4    |    1.12646| * X +  |   -.07433 |   PPM
BEK.CO     |    1.01638| * X +  |   -.08711 |   PPM
DIAL 1/3   |  -19.56100| * X +  |   -.01408 |   ROTAT
DIAL 2/4   |   -4.77980| * X +  |   -.01329 |   ROTAT
```

Printout of Transfer Coefficients When Applied to the Voltage Output of the Instruments Yields the Measured Gas in Engineering Units (PPM). These Coefficients are Updated Automatically During Recalibration Procedures.

$$y = \overset{m}{m}x + \overset{b}{b}$$

where

y is the concentration in ppm
x is the voltage output of the instrument

Printout of the
Voltage Measured on the
65 Channels of the
Data Acquisition System

```
FEBRUARY 20, 1973        16:45 HOURS
  -.106  -.106  -.001  -.003   .001   .000   .802   .037   .027  -.750
  -.123  -.782   .000   .002   .639 15.026-15.076  -.000  -.003   .000
  -.026   .004  -.029   .026   .017   .038   .010  -.025   .003   .033
   .006   .003   .022   .000  -.000   .088  -.010   .200  2.041   .102
   .009  -.003   .000  -.001  -.001  -.106  -.896  -.896  -.896  -.107
  -.106  -.106  -.106  -.610  -.106  -.106  -.106  -.106  -.106  -.512
  -.514  -.513  -.513  -.514  -.513
MEL. NO     $$$$$$$$$$ L   PPM
MEL.NO2     $$$$$$$$$$ L   PPM
MEL.NOX     $$$$$$$$$$ L   PPM
BEN. NO          .0127     PPM
BEN.NO2          .0082     PPM
BEN.NOX          .0187     PPM
BEN.O3           .0463     PPM
BEN.SO2         -.0006     PPM
TRAC.TS          .0056     PPM
TRAC.H2S         .0004     PPM
TRAC.SO2         .0000     PPM
MEL.SO2          .0023     PPM
BEK.THC          .0351 T   PPM
BEK.CH4         -.0041 T   PPM
BEK.CO           .0798 T   PPM
BEK.THC         1.9071 T   PPM
BEK.CH4          .0407 T   PPM
BEK.CO          -.0783 T   PPM
DIAL 1/3        -.0031     ROTAT
DIAL 2/4        -.0000     ROTAT
```

Printout of up to 20 Instruments.
Output in Engineering Units.
$$$ Indicate Instrument Output Is
Offline.

Hourly Averages
Printed Once per Hour Automatically

```
*****************************************************************************************************

R.T.I. INSTRUMENT EVALUATION STUDY

FEBRUARY 20, 1973

           BEN.SO2   TRAC.TS   TRAC.H2S   TRAC.SO2  MEL.SO2   BEK.THC   BEK.CH4
 TIME        PPM       PPM       PPM        PPM       PPM       PPM       PPM
   15 0     .001      .007     -.000       .000      .004     .037T    -.002T
   15 5     .001      .008      .000       .002      .005     .038T    -.001T
   1510     .002      .009      .000       .002      .005     .038T    -.002T
   1515     .001      .009      .000       .004      .004     .039T    -.002T
   1520     .000      .008      .000       .000      .004     .037T    -.003T
   1525     .001      .008     -.000      -.000      .004     .037T    -.002T
   1530     .000      .009      .000       .000      .004     .038T    -.001T
   1535     .001      .008      .000       .002      .005     .038T    -.003T
   1540     .001      .008     -.000      -.000      .005     .038T    -.003T
   1545     .001      .009      .000       .002      .005     .037T    -.004T
   1550     .001      .008      .000       .002      .004     .037T    -.003T
   1555     .001      .008      .000       .002      .004     .037T    -.002T

AVERAGE     .001      .008      .000       .001      .004    $$$$$$$   $$$$$$$

*****************************************************************************************************
```

Code for Status of Instrument
(Blank for Ambient Air Data Point)

$$$ - Indicates Less Than 9
Valid Data Points During Past
Hour, Hence No Average Is Computed

Hourly Averages
Printed Once per Hour Automatically

```
*************************************************************************************
```

Code for Status of Instrument
(Blank for Ambient Air Data Point)

```
R.T.I. INSTRUMENT EVALUATION STUDY

FEBRUARY 20, 1973

           MEL. NO   MEL.NO2    MEL.NOX    BEN. NO  BEN.NO2  BEN.NOX  BEN.O3
  TIME       PPM       PPM        PPM        PPM      PPM      PPM     PPM
  15 0   $$$$$$$L  $$$$$$$L  $$$$$$$L      .013     .005     .017    .047
  15 5   $$$$$$$L  $$$$$$$L  $$$$$$$L      .014     .006     .018    .048
  1510   $$$$$$$L  $$$$$$$L  $$$$$$$L      .013     .007     .019    .047
  1515   $$$$$$$L  $$$$$$$L  $$$$$$$L      .013     .009     .020    .046
  1520   $$$$$$$L  $$$$$$$L  $$$$$$$L      .015     .006     .018    .048
  1525   $$$$$$$L  $$$$$$$L  $$$$$$$L      .013     .004     .018    .048
  1530   $$$$$$$L  $$$$$$$L  $$$$$$$L      .012     .005     .017    .047
  1535   $$$$$$$L  $$$$$$$L  $$$$$$$L      .014     .007     .019    .046
  1540   $$$$$$$L  $$$$$$$L  $$$$$$$L      .012     .006     .018    .046
  1545   $$$$$$$L  $$$$$$$L  $$$$$$$L      .013     .007     .018    .046
  1550   $$$$$$$L  $$$$$$$L  $$$$$$$L      .013     .008     .019    .046
  1555   $$$$$$$L  $$$$$$$L  $$$$$$$L      .013     .008     .019    .046

AVERAGE  $$$$$$$   $$$$$$$   $$$$$$$       .013     .007     .018    .047
```

$$$ - Indicates Less Than 9
Valid Data Points During Past
Hour, Hence No Average Is Computed

```
*************************************************************************************
```

Hourly Averages
Printer Once per Hour Automatically

```
****************************************************************************************

R.T.I. INSTRUMENT EVALUATION STUDY

FEBRUARY 20, 1973

         BEK.CO     BEK.THC    BEK.CH4    BEK.CO     DIAL 1/3  DIAL 2/4
TIME      PPM        PPM        PPM        PPM        ROTAT     ROTAT
 15 0     .080T     4.534T     3.942T     -.088T     -.003     -.000
 15 5     .079T     4.560T     3.908T     -.087T     -.003     -.000
 1510     .081T     4.599T     3.919T     -.089T     -.003     -.000
 1515     .083T     4.603T     3.919T     -.088T     -.003     -.000
 1520     .082T     4.631T     3.897T     -.088T     -.003     -.000
 1525     .080T     4.660T     3.874T     -.088T     -.003     -.000
 1530     .080T     4.667T     3.885T     -.088T     -.003     -.000
 1535     .084T     4.693T     3.885T     -.088T     -.003     -.000
 1540     .083T     4.720T     3.863T     -.088T     -.003     -.000
 1545     .082T     4.712T     3.863T     -.087T     -.003     -.000
 1550     .080T     4.742T     3.908T     -.088T     -.003     -.000
 1555     .079T     4.740T     3.863T     -.088T     -.003     -.000

AVERAGE  $$$$$$$    $$$$$$$    $$$$$$$    $$$$$$$    -.003     -.000

****************************************************************************************
```

Code for Status of Instrument
(Blank for Ambient Air Data Point)

$$$ - Indicates Less Than 9
Valid Data Points During Past
Hour, Hence No Average Is Computed